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IN THIS ISSUE

Suspending Action by Detergents in the Presence of Substrate. *Jay C. Harris* 99

A Simple Ballooning Yarn Apparatus. *D. Brunnschweiler and I. S. Mohammadain* 119

National Cotton Council
Chemical Finishing Conference

Formic Acid Colloid of Methylolmelamine as a Weather and Rot Resistant Finish for Cotton. *W. Norbert Berard, Gloria A. Gautreaux, and Wilson A. Reeves* 126

Study of Improvement of Smoothness of Cotton Fabrics. *Charles Goldthwait, Rosa D. Kirby, Sam Fretwell, and Hans Wichart* 134

Fiber Structure and Mechanical Properties of Untreated and Modified Cottons. *Rollin S. Orr, Lloyd B. DeLuca, Albert W. Burgis, and James N. Grant* 144

Permanent Set in Cotton and the Physical Mechanism of Wrinkle Resistant Treatments. *Mason DuPré, Jr.* 151

Imparting Crease Resistance and Crease Retention to Cotton With APO. *George L. Drake, Jr. and John D. Guthrie* 155

Bleaching of Cottons in Home Laundering. *R. H. Fink* 165

Triazones—Creaseproofing Agents for Cotton. *R. L. Wayland, Jr.* 170

Performance Characteristics of a New Triazine-Formaldehyde Based Cross-Linking Agent for Cellulosic Fabrics. *T. F. Cooke and P. B. Roth* 180

LETTER TO THE EDITOR

Effect of Twist in Mercerization of Single Yarn. *A. G. Chitale and S. V. Gokhale* 191

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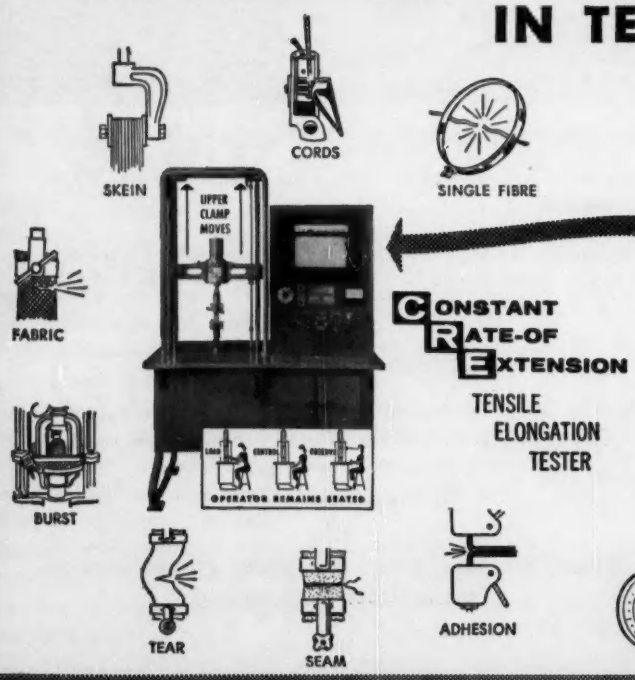

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Suspending Action by Detergents in the Presence of Substrate

Jay C. Harris

Monsanto Chemical Company, Research and Engineering Division, Research Department, Dayton, Ohio

EVEN IF a selected cleaning system were comprised of single-component soil, substrate, and detergent solution, and all were essentially pure, the system is far from "simple." Interactions between substrate and soil, substrate and detergent solution, soil and detergent solution, and of the three phases [36, 77] occur, and are difficult to measure. It is understandable why many investigators have attempted measurements in the absence of substrate, but lacking substrate the system is incomplete, and for such a dynamic system as a cleansing operation leaves much to be desired. The present discussion is concerned more with the mechanisms involved in maintaining soil in suspension (preventing deposition or redeposition) in detergent solutions than in soil removal from the substrate.

Soil–Detergent Solution Systems

Previous discussion of suspending action by detergent solutions has related the ability of detergent systems to prevent the sedimentation of soil particles. Reich [46] rightly distinguishes between specific sedimentation (or suspending value), which has relatively little to do with soil redeposition on a substrate; protective action, which prevents particles from adhering to the substrate; and an actual dispersion or redeposition preventive mechanism, operative in dynamic systems where the soil is deflocculated and the particles have lowered mutual attraction. However, it seems certain that even though previous investigators have indirectly utilized the sedimentation technique, this has not been in a specific sense, but as a relative measure of differences in a static (versus a dynamic) system.

Preferential sorption of ions of the suspending agent increases the particle charge or zeta potential, resulting in deflocculation of aggregates of primary particles. This deflocculating effect may be of relatively lesser importance when compared with the mechanical forces involved in the cleaning operation [46], but nevertheless is effective in preventing soil redeposition.

Soil–Substrate Systems

Soils adhere to substrates by several mechanisms.

Mechanical forces may be exemplified as those which operate when a soil particle is entrapped in the interstices of a fabric and can be removed by mechanical means [53]. Intermediate between mechanical forces and those forces which more generally are considered as controlling factors in soil retention and removal are macro-occlusion (entrapment of soil particles in intra- and inter-yarn spaces) and micro-occlusion, or entrapment of soil particles in the small irregularities of fiber surfaces [9].

Chemical forces [53] which attach soil to sub-

strate are said to operate through ionic or hydrogen bonding, and stains may be considered as of this class.

Electrical forces which cause attraction of soil for substrate may be electrostatic, in which soil for substrate attraction is considerable, and results from dissimilarity of charge of considerable magnitude; van der Waals' or coulombic forces, which operate within molecular ranges; and electrokinetic forces largely associated with the double layer surrounding soil-substrate in aqueous systems.

The polarities of the substrate and soil can have considerable effect upon soil tenacity and can affect the ease of cleaning and possibly the degree of redeposition. The water retaining capacity of fibers [30] varies, and may be considered an indication of their polarity:

Fiber	Approx. water holding capacity, %
Perlon (amide)	13
Acetate rayon	27
Wool	42
Cotton	45
Viscose rayon	95

Soils can vary from hydrophilic manganese dioxide to highly hydrophobic carbons or mineral oil.

Particle Size and Particle Size Distribution

Other factors which obviously exert influence on the detergent system are the rugosity of the substrate, its size, and the particle size and particle size distribution of the soil. Soils from Los Angeles smogs, for example, range downward from 1.5 μ [51]. The particle size distribution of an average of natural dirts from six large U. S. cities [50] and a synthetic dirt is shown in Table I. Difficulty has been encountered in securing soil samples on which particle size determination may be made, but information on this general subject [15] indicates that atmospheric dust particles have a mass median diameter of about 1 μ; vacuum cleaner dirt from carpets, 0.3–35 μ; the soil retained on pile fibers, 0.2–4 μ; while organic contaminant particles ranged from 0.5 to 5 μ in diameter.

The effect of carbon particle size on soil retention in chopped cotton fiber [9] is shown in Table II. The work in Table II was amplified by testing 13 carbon blacks of primary particle size 13–120 mμ; shown in Figure 1 are data for effect of particle size on reflectance from cotton fiber. That these general data [21] carry over with certain exceptions to other fibers is shown in Figure 2.

Compton and Hart [10A], in discussing mechanisms in the binding of soils to fabric, very rightly showed that three main categories existed: entrapment of particles in intra- or inter-yarn spaces, called macro-occlusion; entrapment in fiber surface irregularities, called micro-occlusion; and sorptive bonding of soil to fiber through coulombic or van der Waals' attractive forces. Of these three, they considered macro- and micro-occlusion major factors [22].

Though carbon blacks may have very small individual particle sizes, they more frequently are found as agglomerates of varying sizes. Kling [31], in some beautiful electron micrographs, has shown this agglomeration with India ink, carbon, and iron oxide. Even on cotton surfaces, dry soil appeared in the agglomerated form. A further series of micrographs showed various soils on another series of fibers [28].

Kling and Mahl [29] were able to detect increase in lightness of soil shade under the electron microscope as related to the number of soil particles apparent. Macroscopic cleanliness was apparent when no more soil particles could be detected under the electron microscope. While coarser particles are easier to remove than fine ones, they become more difficult to remove as their diameter becomes less than 0.2 μ. Migration of soil into the interior of cotton or wool fiber was not found to occur.

TABLE I. Soil-Particle Size Distribution [50]

Size distribution	Natural, %	Synthetic, %
<4 μ	53	68
4–8	8	16
8–12	7	8
12–16	8	4
16–20	7	2
>20	17	2

TABLE II. Particle Size and Soil Retention [9]

Black	Primary particle size, mμ	Reflectance, %
Germantown lampblack	100	44
Molacco black	80	27
Aquablak B (paste)	30	10
Neo Spectral black	10	4

Reich [46] found that deflocculation (reduction of agglomerate particle size) was the controlling factor in preventing deposition of carbon or of ferric oxide on fabric surface. The effect of agitation (mechanical cleaning action) was investigated by him; he observed that the more intense the agitation, the smaller will be the average particle size and the more rapidly equal floc size is approached. At any given agitation intensity level the average floc size will increase with increased concentration of the disperse phase, the reasoning being analogous to that leading to the law of mass action in chemical reaction. Dispersion breakdown to smaller floc size proceeds at a rate independent of soil concentration.

Rhodes and Brainard [48] found that extended washing times resulted in a pronounced decrease in suspending action, which they attributed to an increase in the degree of dispersion of the soil.

Vold and Phansalkar [72] pointed out that if micro-occlusion were the controlling factor, it would be expected that the average carbon particle aggregate size in the suspension from which deposition occurred would play an important role, since smaller particles would penetrate pores and other capillary spaces in the fiber or fabric. Their data showed no marked change in carbon deposited where aggregate size was decreased greatly; also, no direct relation existed between degree of deposition and aggregate size distribution in the suspension.

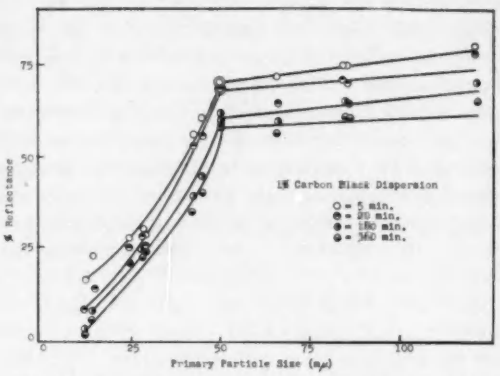

Fig. 1. Effect of soil primary particle size on rate of change of reflectance [19].

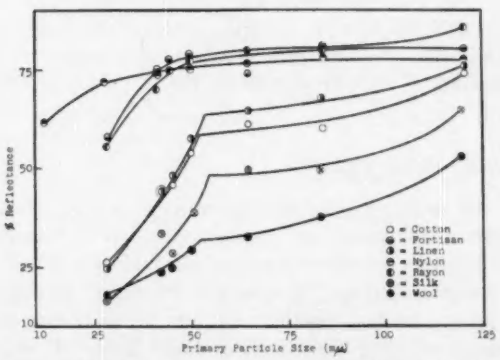

Fig. 2. Reflectance vs. soil particle size; various fibers [21].

The mechanical, chemical, and electrical forces that affect redeposition of soil on substrate are in turn affected by soil and substrate polarities, particle size, and particle size distribution. Carbon soil particles seldom are found as discrete individuals, but as agglomerates of varying size; this frequently is true of other soils. Though some work has indicated no direct relationship between degree of deposition and aggregate size distribution in suspension, sufficient evidence exists to believe that deflocculation or reduction in size of original flocs to an optimum small size will aid in preventing soil redeposition. Indeed, some reports indicate this as the main function of surfactants.

Contrary to some authors, others have found convincing evidence that soil does not migrate to the interiors of fibers and indication that penetration by micro-occlusion of small particles is quite unlikely to occur.

Methods of Investigation

The obvious methods for introduction of soil to the solution and substrate are either to add a soil to the detergent system containing the substrate or to wash clean substrate in the presence of soiled material. However, fabric structure can radically change apparent results, and a simplified structure may be desired; the ultimate would be individual fiber particles. An example of the latter is the "chopped fiber" technique, where the fabric or yarn is reduced to very short lengths. A tracer technique has been used in which tagged carbon was employed, electrophoretic and sedimentation values have been determined, and visual examination by electron micrography has been utilized.

Chopped Fiber Technique

Minimization of the effect of fabric or yarn structure upon the uniformity of redeposition of soil (degree of suspendability) upon fiber was initiated by Kornreich [32]. Though Kornreich was interested

in sericin removal from raw silk, the general procedure appealed to Powney and Feuell [44], who reduced cotton fabric to individual short fibers and soiled them with synthetic dirt.

Compton and Hart [9] prepared kiered and bleached cotton fiber in 100–1000 μ lengths by passage through a Wiley mill. Their soil suspension tests were made as follows. The soil was comprised of carbon black (several, of well defined particle size, were used), 1.0 g.; Daxad (polymerized alkylaryl sodium sulfonate, a surfactant), 0.05 g.; and water, 99 g.; all homogenized in a Premier mill. The fiber was slurried with soil dispersion in sufficient quantity to give 10% of soil solids based on fiber weight. This slurry was stirred gently in the presence or absence of additives, loose soil decanted until the supernatant water was clear, a pad made on a Büchner funnel, the pad dried, and the reflectance measured directly photometrically.

Later papers by these same investigators [19, 20, 21] utilized not only cotton but linen, silk, wool, nylon, viscose rayon, and Fortisan. In certain of these cases a somewhat different technique was used. The soil–fiber slurry was stirred and decanted until a clear supernatant liquor was obtained. The slurry was then reclassified in a Waring Blendor, the procedure consisting of 10 sec. stirring (10,000–12,000 r.p.m.), 10 sec. standing, then 20 sec. stirring. Decantation was repeated until a clear supernatant liquor resulted, the slurry was passed through a Büchner funnel to form a pad, this was dried, and reflectance was measured photometrically.

Soil Addition Technique

Simple addition of soil to a detergent solution offers the most direct means for introducing the soiling factor into a suspension test. It has the advantages of gravimetric control, control of particle size and agglomeration, and does not necessarily depend upon previous treatment or the nature of a complicated medium (such as a soiled fabric).

Carter [7] early recognized the advantages of these systems and explored the addition of "soils" such as ferric oxide, carbon black, raw umber, burnt umber, yellow ochre, vermilion, and others. Stock suspensions of these were prepared and the ability of detergent solutions to prevent their deposition on cotton sheeting was estimated under controlled conditions of agitation.

A Navy specification [39] utilizes a mixture of a synthetic city soil [50] with a carbon black as the soiling medium, but evaluation is made on the basis of multicycle operation. A single cycle comprises a 10-min. wash of white fabric in detergent solution containing the soiling suspension, two machine rinses of 3 min. each, followed by damp-drying and finally iron drying between cotton fabric. The second cycle repeats the first except for the absence of soil. A complete test would comprise four runs with soil and three without ($3\frac{1}{2}$ cycles).

Powney and Noad [43] utilized a special shaking device in which the frequency could be varied to measure the deposition on cotton fabric of air-floated ilmenite black from detergent solutions by reflectance measurement. The same conditions were adopted by Wagg [74], except that he designed a frame to prevent fabric wrinkling, slightly changed the dimensions of the vessel, and operated at 60° C.

An approach by Phansalkar and Vold [42] designed to permit estimation of the average size of agglomerates of Sterling NS carbon (75 mμ, deoiled) while measuring quantitatively its deposition on fabric, utilized a radio isotope tracer adsorbed on the carbon. This particular work could have been improved by control of agitation and temperature and longer duration of exposure. Stüpel [60] performed his experiments in porcelain dye beakers, stirred in a gang of eight to control the agitation, using standard Micronex as the suspended pigment. In this case alkylnaphthalene sulfonate was used with the black to permit evenness of dispersion. To control both temperature and agitation, Ross and coworkers [49] used closed Dewar flasks clamped and agitated in a home washing machine. Weatherburn [75] and his coworkers measured suspending power using a variety of characterized carbons, employing a vacuum bottle and shaker as equipment.

Table III lists the materials and methods used in measuring the suspension values of detergents in preventing their deposition on fabric, generally cotton.

Soiled Fabric Usage

In ordinary washing operations, almost clean articles frequently are washed either with heavily soiled ones or, where a proper classification is used, garments of about the same general degree of dirtiness are washed together. In any event, it may be conceived that, even with a single piece of nonuniformly soiled fabric, as most of the soil is being

removed there may be some redistribution in the washing process to previously unsoiled areas. It is on this basis that a number of tests have been developed.

One considerable difficulty in washing clean fabric with soiled pieces is that no truly constantly available amount of soil is present in the baths, and this quantity changes with the detergent employed. However, on the basis that this occurrence (controlled or not) takes place in normal operations, a series of test methods have been developed. Armstrong and coworkers [1], using corn- or olive oil-Oildag soiled fabrics, sewed four swatches $2\frac{1}{2} \times 2$ in. in size to the same number of white swatches and washed them at 120° F. in 100 ml. solution, adding 15 stainless steel balls to the Launder-Ometer jars. Various times of washing were observed, and reflectance measurements were utilized for comparison. A somewhat similar test was used by Utermohlen and Ryan [64].

Sanders and Lambert [50] used swatches of fabric soiled with a synthetic natural soil standardized upon a multicycle procedure to measure redeposition (or prevention of soil deposit). Bernstein and Sosson [5] used a full scale test method for measurement of redeposition in which ballast loads of normally soiled garments were used. Vaughn and coworkers [70] arrived at the conclusion that multicycle tests were necessary for satisfactory measurements, and Bernstein and Sosson [6] proved the unreliability of a single cycle and found 10-cycle washings satisfactory.

In general, less reliance has been placed on soiled cloth addition to a laboratory evaluation for whiteness retention or redeposition, but practical testing utilizes this technique almost exclusively; in any event, more than a single cycle is necessary for satisfactory evaluation.

The equipment used for controlling the degree of agitation varies all the way from hand dipping to the use of machines and containers devised to vary and control temperature and agitation over a broad range. Intermediate are standard laboratory washing devices such as the Launder-Ometer, Terg-O-Tometer, and the Determeter. The effect of degree of agitation in apparent effect on deposition will be discussed elsewhere.

In only one respect is a near approach to agreement reached—that of measurement by reflectance. The lack of effective quantitative measurement afforded by reflectance will be discussed in detail in another section.

The broad range of ratios of soil/solution, fabric/solution, and soil/fabric indicates the lack of agreement in reasoning concerning these tests, and relatively few tests were made under conditions which approximate those encountered in actual washing operations.

TABLE III. Addition of Soil for Suspension Measurement

No.	Suspended materials	Washing device	Temp., °C.	Time, min.	Rating: Soil/Soln.	Rating: Fabric/Soln.	Ratio Soil/Fabric	Measurement	Ref.
1	Ferric oxide, carbon black, raw and burnt umber, yellow ochre, vermilion	Launder-Ometer	60	30	0.01			Reflectance	7
2	City soil plus Aquadag	Terg-O-Tometer	60	40				Reflectance	39
2A	Raw umber or ferric oxide	Launder-Ometer	60	20	0.01	0.00375	2.3		37
3	Air-floated ilmenite	Special shaker	—	20	0.16	0.0006	2.5	Reflectance	43
4	Sterling NS Carbon radiotracer tagged	Dipping by hand		1	0.0025 to 0.005	0.0017	3	Geiger Counter	42
5	Standard Micronex	Gang washer	95	60	0.1	0.4	4	Reflectance	60
6	Aquadag	Dewar flask in wash machine	49	10	0.0003	0.11	0.027	Reflectance	49
7	Various blacks	Vacuum bottle and shaker	60	20	0.001	0.034	0.03	Reflectance	75
8	Mogul A	Deter-Meter	60	10	0.000003	0.0002	0.014	Reflectance	38
9	Aquadag	Terg-O-Tometer	49	10	0.00011	0.015	0.0073	Reflectance	57
10	Aquadag	Terg-O-Tometer	43	20	0.00011	0.0045	0.024	Reflectance	71
11	Aquadag	Launder-Ometer	60	20	0.00022	0.0375	0.006	Reflectance	17
12	Sterling NS Carbon	Dipping by hand	—	1	0.005	0.0017	3	Reflectance	73
13	Aquablak B	Launder-Ometer	60	20	0.002	0.035	0.029	Reflectance	13
14	Aquablak B	Launder-Ometer	60	5	0.0007	0.01	0.07	Reflectance	68

Sedimentation

Most of the suspension tests have depended upon differences in the rate of sedimentation to indicate possible differences in preventing redeposit of soil particles upon a substrate. Technically, gravitational or sedimentation effects are essentially absent in the dynamic systems represented in detergent operations. An optimum degree of agitation is maintained to permit flexing or mild abrasion of the surface to be cleaned, either by surface-to-surface contact or by impingement of cleaning solution.

Stabilized dispersed soil in solution may be estimated by a decrease in the rate of sedimentation of the soil. Fong and Ward [14] ultracentrifuged carbon black suspensions to measure sedimentation rates, shown in Table IV as Svedberg units $\times 10^{-13}$ sec.

Uncharged hard carbon particles of 28 mμ average diameter are computed to have a sedimentation constant of 320 S. The observed rates corresponded to spheres about 56 mμ diameter or to slightly more massive particles of irregular shape. Clusters of eight 28-mμ particles sedimenting together would have approximately the maximum rate observed. Decrease in sedimentation rate from 1,330 to 860 S corresponded to halving the mass of the sedimenting unit—in effect deflocculating the suspension.

It is obvious that collision of substrate with suspended soil particles or agglomerates, or particle with particle, would bring into play forces which under static conditions might seldom occur. Under these circumstances, van der Waals' forces might become effective. Sorptive effects can be initiated more effectively in dynamic systems. Any mechanism which can cause flexing can cause marked changes in the substrate. Higher temperatures will increase activity and increase rate of contact even if no mechanical energy is involved. Though these are persuasive arguments, conditions which will cause suspensions to remain stable for long periods of time are not to be neglected. Factors which can promote stabilized suspensions are desirable zeta potential, absence of flocs, optimum particle size, and forces of repulsion of particle for particle. Some of these factors are responsible for stable detergent systems which permit rinsing away of removed soil. Until the detergent process is better defined, suspension tests may find specific application.

TABLE IV. Sedimentation Rates [14]

	Sedimentation constant, S $\times 10^{-13}$ sec.
Water	1350
1. Sodium tripolyphosphate: 0.08% Sodium carbonate: 0.04%	1130
2. 1 above + 0.12% Nacconol NRSF	1140
3. Carboxymethylcellulose	860

Measurement of Deposited Soil

An essentially universal estimate of soil on substrate is made by reflectance measurement. Differences in whiteness (reflectance) are apparent to the eye, and small amounts of soil evenly (or unevenly) distributed over a surface are visual evidence of lack of cleanliness. Desirable would be a quantitative measurement of soil deposited, and reflectance would become a valuable direct measurement if it could be shown that a quantitative relationship existed.

Bacon and Smith [2] applied the Kubelka and Munk equation [34] to the problem of relating reflectance to the quantitative amount of soil remaining on fabric surfaces:

$$K/S = \frac{(1 - R)^2}{2R} \qquad (1)$$

where K = coefficient of reflectivity, S = coefficient of light scattering, and R = observed reflectivity for monochromatic light; they calculated the percent removal of black from their soiled fabric through its use:

$$\frac{K/S \text{ for soiled fabric} - K/S \text{ for scoured fabric}}{K/S \text{ for soiled fabric} - K/S \text{ for unsoiled fabric}} \times 100 = \text{percent black removed} \qquad (2)$$

Their equation for detergency, which at that time was still under investigation, was written as:

$$S = K(CFT)^n \qquad (3)$$

where S = percent soil removal, K = a constant, n = constant slope, C = concentration, F = force applied, and T = time. The equation applied to the linear portions of their logarithmic detergency curves, but these linear portions fell below ordinary use–concentration conditions for most detergents.

Since reflectance measurements as a calculation of brightness regained are used rather generally by industry, Reich, Snell, and Osipow [45] investigated

the Kubelka-Munk equation as applied to soiled fabrics. They concluded that reflectance of soiled cloth can be correlated to the amount of soil present by the equation:

$$\log\left[\frac{(1-R)^2}{2R} - \frac{(1-R')^2}{2R'}\right] = n \log G + \text{constant} \quad (4)$$

where R = reflectance of soiled cloth, R' = reflectance of clean cloth, and G = amount of soil present. However, they indicated that n (the slope) during washing was frequently 1 (and the equation became the Kubelka-Munk) but that during artificial soiling (and agglomeration of soil) it had a value of 0.65–0.7.

Hart and Compton [22] demonstrated that the Kubelka-Munk equation frequently failed when applied to reflectance systems because of particle distribution, orientation, and specific absorbence. Provided that the specific absorbence of a pigment for the fabric system is essentially constant, Equation 2, Bacon and Smiths', can be used, but if the specific absorbence varies, this must be determined. Hart and Compton calculated change in specific absorbence:

$$(K/S)_T = (K/S)_{WF} + (K/S)_{RS} + (K/S)_B \quad (5)$$

where $(K/S)_T$ = total K/S value after washing, $(K/S)_{WF} = K/S$ value for soiled and washed swatches, $(K/S)_{RS} = K/S$ value for redeposit swatches, and $(K/S)_B = K/S$ value for bath liquor. Then

$$\left[\frac{(K/S)_T}{(K/S)_{SF}} - 1\right] \times 100 = \text{percent change in specific absorbence} \quad (6)$$

in which $(K/S)_{SF} = K/S$ value for the original soiled swatch. Factors of fabric and yarn structure, nonuniformity of soil distribution, and orientation were obviated by using a chopped fabric technique.

Quantitative analysis of deposited soil on textile fabrics for correlation with reflectance was carried out by Utermohlen and Wallace [63], who found good agreement at a medium soiling range when iron oxide pigment was used. However, Reich and coworkers [40] showed that the K/S linear relationship held only at low soil values. The same conclusion was reached by Strauss [58].

The graphite content of soiled and washed fabrics was quantitatively estimated by Harris, Sullivan, and Weeks [18] by dissolving the fabric away from the graphite, then determining the latter turbidimetrically. In the working range, and particularly for higher reflectances, they found the K/S value for colloidal graphite on cotton to be essentially a linear function of graphite concentration.

Previous discussion has indicated the considerable changes in particle characteristics which can occur in the washing operation. Some materials more

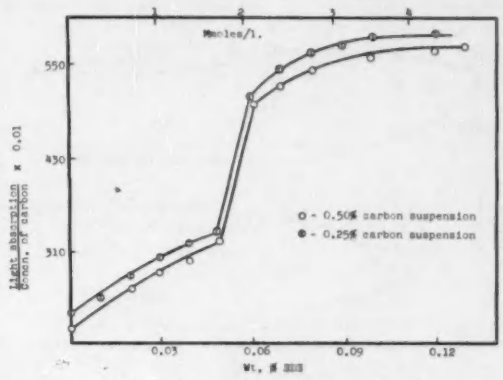

Fig. 3. Effect of sodium dodecyl sulfate on size distribution of suspended carbon [42].

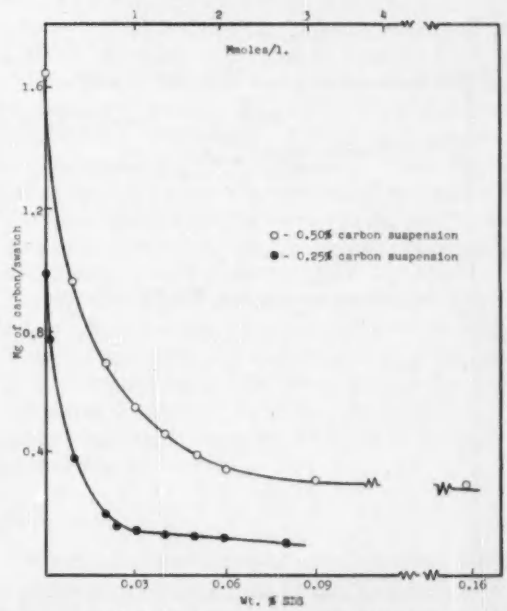

Fig. 4. Weight of carbon deposited on cotton from sodium dodecyl sulfate solutions [42].

than others will form agglomerates, or will be dispersed to a greater or lesser degree in detergent systems. Carbonaceous soils appear to be affected considerably in this respect. A radiotracer technique worked out by Phansalkar and Vold [42] for tagging defatted Sterling NS Carbon was used to investigate the Kubelka-Munk relationship. Their work showed that the Kubelka-Munk equation failed to account for reflectance values obtained. The apparent blackness as measured by reflectance depended upon both the quantity and subdivision of the carbon deposit; the lower the reflectance the more finely dispersed was the carbon found to be. Their data, Figure 3, show that small concentration changes of sodium dodecyl sulfate had little effect on carbon particle size distribution, greatly decreased the amount on the fabric, and markedly increased reflectance. On continued addition of surfactant, a concentration was reached where the carbon weight deposited decreased only slightly. With further surfactant concentration, increase in the average size of the suspended (and presumably) the deposited carbon aggregates decreased markedly, reflectance decreasing with increasing surfactant concentration in this range even though the amount of carbon deposited decreased slowly (Figure 4).

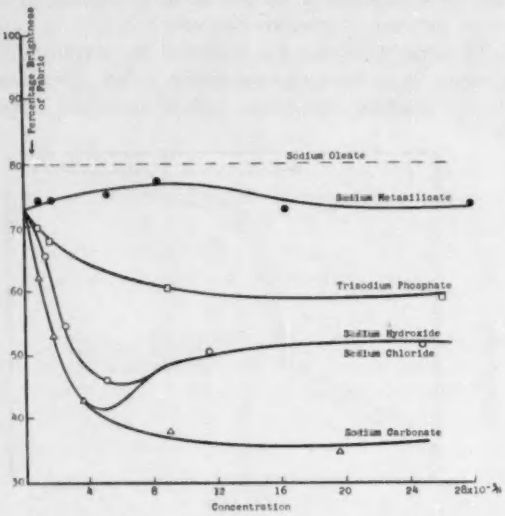

Fig. 5. Deposition of ilmenite on cotton fabric at 22° C. [43].

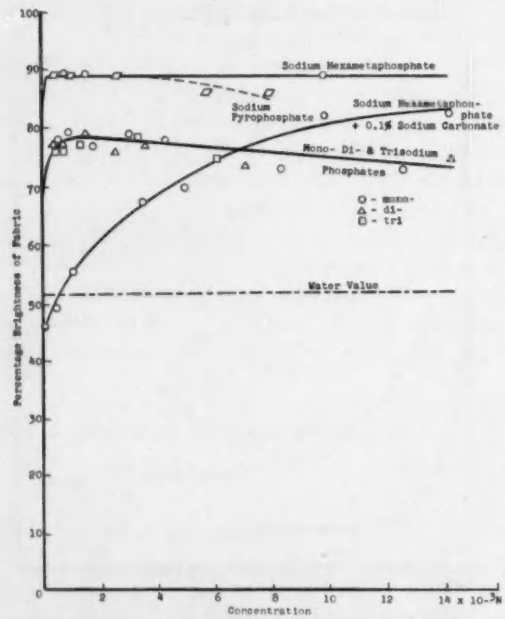

Fig. 6. Suspending power of phosphates [43].

Reflectance values are rather directly related to particle size; the smaller the individual particle, the greater the dispersion of incident light. For white particles, subdivision would result in apparently greater reflectance, while for black particles, the smaller the size (and more even the distribution), the greater the absorbence of incident light. Reflectance is the visual estimate of whiteness or cleanliness, and so long as no better quantitative method for estimation is available, reflectance methods probably will continue in use. Several applications of the Kubelka-Munk equation have been successfully made at low soil levels, where size distribution of the suspended solid does not change appreciably. Hence it may be that for redeposition values which approach levels encountered in practice, reflectance values may be quite valid.

Soil Suspension Data

Builders

Powney and Noad [43], using ilmenite as a soil, found considerable differences in the effects produced by electrolyte builders upon the stability of soil suspensions, as evidenced by fabric brightness. In increasing order of effectiveness the builders were sodium carbonate < sodium hydroxide-NaCl < water < sodium metasilicate < trisodium (mono-, di-ortho) phosphate < sodium oleate < hexameta-

phosphate plus sodium carbonate < tetrasodium pyrophosphate < sodium hexametaphosphate (see Figures 5 and 6).

Increase in deposition by sodium carbonate or caustic soda is attributed to sodium ion effect rather than to the effect of pH. The considerable protective action of silicates and phosphates is attributed to selective adsorption of the anion, the polyphosphates exerting protective action at concentrations as low as 5–10 p.p.m.

Carter [7], using a variety of pigments, found that except for silicates and trisodium phosphate, alkaline electrolytes showed little or no ability to prevent soil deposition on fabric; trisodium phosphate was placed intermediate between the silicates and simple alkalies.

Weatherburn et al. [76] were unable to show marked ability of builders to suspend carbon, though others had been successful with more polar soils. The optimum suspension ability occurred at concentrations of 0.005% or lower, and decreased even over distilled water at higher concentrations. In this connection, the familiar effect on carbon particle mobility when the double layer is depressed by excess of sodium ion should be recalled.

Merrill and Getty [37] determined the deposition prevention of three soils—iron oxide, raw umber, and ilmenite—by a series of builders with the following results, the materials arranged in order of decreasing effectiveness:

Iron oxide	Raw umber	Ilmenite
Tetrasodium pyrophosphate	Tetrasodium pyrophosphate	Tetrasodium pyrophosphate
$Na_2O \cdot 2.1\ SiO_2$	$Na_2O \cdot 2.1\ SiO_2$	$Na_2O \cdot 2.1\ SiO_2$
$Na_2O \cdot 2.9\ SiO_2$	Trisodium phosphate	$Na_2O \cdot 2.9\ SiO_2$
$Na_2O \cdot 3.3\ SiO_2$	Na_2SiO_3	Na_2SiO_3
Trisodium phosphate	Na_2CO_3	Trisodium phosphate
Na_2SiO_3	NaOH	Na_2CO_3
Na_2CO_3		NaOH
NaOH		

Combinations of tetrasodium pyrophosphate with silicates were improvements over pyrophosphate-carbonate or silicate-carbonate mixtures for either iron oxide or ilmenite soils. Carter and Stericker [8] determined the redeposition values for various sodium silicates in suspending carbon black, burnt and raw umber, and ferric oxide.

Stüpel [60] investigated three phosphates and found very low levels of effectiveness for all three, the pyro and tripoly being essentially equal in effect and both better than the hexametaphosphate.

TABLE V. Soil Deposited on Fabric in Builder Solutions [71]

	Units soil deposited		
	Concentration salt, %		
	0.05	0.30	0.55
Sodium carbonate	48.8	55.8	55.5
Sodium metasilicate	40.7	47.8	46.0
Tetrasodium pyrophosphate	46.9	55.6	56.5
Sodium tetraborate	46.8	54.5	56.0
Sodium chloride	57.9	57.2	58.8

TABLE VI. Soil Deposited [71]

	Units soil deposited
	0.10% Organic detergent
A *	6.6
35% A—65% Na_2SO_4	25.6
Sodium oleate	4.4
35% Sodium oleate—65% Na_2SO_4	14.5
35% A—65% Sodium carbonate	19.5
35% A—65% Tetrasodium pyrophosphate	17.7
35% A—65% Sodium metasilicate	13.8

* A = pure anionic detergent; sodium salt of sulfated cocoanut monoglyceride.

Vitale [71] measured the Aquadag deposited on fabric in the presence of varying concentrations of builder salts (Table V) and demonstrated that increasing concentration above 0.05% increased the amount of soil deposited. Of the five materials tested, sodium metasilicate was the least offensive in this respect, but nevertheless caused deposition. He concluded that water-soluble inorganic electrolytes, whether sodium or calcium/magnesium types (from water hardness), all tended to cause deposition.

Table VI shows that builder salt addition to solutions of either a sulfated monoglyceride or to sodium oleate increases the soil deposited during the test [71]. This investigator also demonstrated that even surfactants not forming insoluble salts in hard water need protection, achieved by the addition of calcium ion suppressants.

Surfactants

The characteristic action of sodium dodecyl sulfate to reduce deposition of carbon upon a fabric was determined by a precise radiotracer technique [42]. The amount of carbon deposited decreased sharply

with increased surfactant concentration, then levelled off at concentrations dependent upon the initial amount of carbon present. The lower the amount of carbon used, the less the amount of surfactant required before a state of near equilibrium was reached.

TABLE VII. Soil Suspension by Pure Surfactants [59]

Standard Micronex Soil

Surfactant	Common name	Soil suspending ability, %
Sodium oleate	Olein Soap	20.2
Polyalkylnaphthalene sulfonate	Supralan Conc.	51.6
Alkyl sulfonate	Mersolat H	58.5
Dodecyl/tetradecyl sulfate	FA-Sulfonat	69.8
Palmitylmethyltaurid	Igepon AP	72.1
Isooctylphenolpolyglycol sulfate	Alipal D	75.0
Higher fatty alcohol sulfate	Gardinol CA	75.5
Oleyl lysalbinate	Lamepon A 44	80.0
Diisopropylnaphthalene sulfonate	Nekal BX	50–53*
Alkyl sulfonate (C_{15}/C_{18})	Mersolat H	59–63
Dodecylbenzene sulfonate	Marlon	60–65
Dodecylphenolpolyglycol ether	Sapogenat A	75–90

* Above this point, 60 mg. of carbon; at this point and below, 20 mg. carbon.

TABLE VIII. Soil Redeposition [1]

Surfactant	Structure	Soil redeposition, %
Ninol 979	Fatty dialkanolamide	3.6
Texscour Soap	Sodium oleate	4.3
Duponol D	Fatty alcohol sulfate	4.8
G–1226	Fatty acid–ethylene oxide adduct	4.8
Igepon A	Fatty acid sodium isethionate	5.5
Katapol CNS	Alkyl polyoxyethylene amine	5.8
Triton NE	Alkylarylpolyoxyethylene ether	6.1
Igepon T	Sodium N-methyl-N-oleyl taurate	6.3
Nacconol NR	Dodecylbenzene sodium sulfonate	6.7
Roccal	Alkyldimethylbenzyl ammonium chloride	11.8

TABLE IX. Suspending Power [10]

(Chopped Fiber Technique)

Surfactant	0.5% Concentration surfactant: Active ingredient, %	Suspending power, %
Sodium N-methyl-N-oleyl taurate	76	36
Sodium alkylaryl sulfonate	100	17
Sodium soap	99	17
Sodium metasilicate	100	−16
Fatty alkylolamide	100	68
Cetylpolyoxyalkylene adduct	100	68
Diethylene glycol monostearate	100	2

Powney and Noad [43] measured the brightness retention capacity of pure soaps and found that for sodium laurate to achieve the optimum brightness of sodium stearate required several hundred times the concentration of the former, due to the difference in effective chain length. Though sodium oleate and stearate have the same number of carbon atoms in the chain, the oleate required a considerably higher concentration to achieve the same brightness, due undoubtedly to the effect of the double bond in reducing the effective chain length.

Figure 7 shows the brightness of fabrics subjected to suspensions of ilmenite soil, in which several surfactants were evaluated for suspending action [43]. The sodium oleate-Gardinol E mixture essentially equals soap alone, while the depressing effect of sodium carbonate is demonstrated with sodium tetradecyl sulfate.

These data seem to indicate that the synthetic surfactants have less ability to suspend soils than soaps, but this statement should be accepted cautiously, since the surfactants tested have generally had about twelve effective carbon atoms in the chain, and even sodium laurate has poorer suspending action than soaps with greater effective chain lengths.

Stüpel [59] has probably produced more data than most other investigators combined; investigated for soil suspension ability using standard Micronex as the soil were the surfactants shown in Table VII. These are arranged in general order of increasing effectiveness, and the relative effectiveness of non-

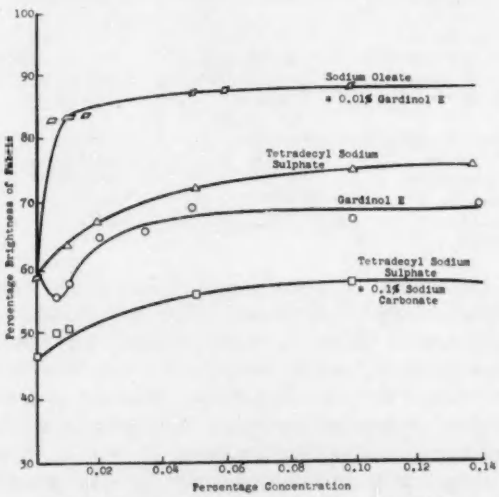

Fig. 7. Suspending power of surfactants [43].

ionics as a class is outstanding. Another series of more extensive tests by Stüpel [60] covered seven different fatty alcohol sulfates, eight different alkylaryl sulfonates, six ethylene oxide adducts, two sulfated ethylene oxide condensates, a fatty acid condensate, an alkyl sulfonate, a secondary alkyl sulfate, and a soap. The outstanding conclusions from this considerable volume of work follow. The most effective surfactants for suspending this soil were the alkylpolyoxyethylene adducts, the higher molecular weight fatty alcohol sulfates, and soap. Least effective were the alkylaryl sulfonates. Combinations of surfactants generally exhibited minima for their mixtures, and in no case was synergism evident.

Armstrong's committee [1] evaluated a series of ten surfactants, with the results shown in Table VIII. The ineffectiveness of the quaternary Roccal could have been expected, but the relative ineffectiveness of the alkylbenzene sulfonate would not necessarily have been anticipated.

Compton and Hart [10], using the chopped fiber technique, evaluated several surfactants, with the results shown in Table IX. The relative effectiveness of the nonionic surfactants of adequate structure is apparent.

Surfactant–Builder Mixtures

Table VI shows the general lowering of effectiveness of surfactant–builder mixtures in preventing soil build-up on fabrics. However, silicates and phosphates tend to cause less deposition than simple electrolytes.

Soap and builder mixtures have been rather extensively investigated. Mixtures of soap and silicate were found better than either alone in preventing the deposition of a variety of soils [7, 8]. The whiteness retention characteristics of mixtures of soap and builders (0.1%:0.1%) against oily carbon gave the following ratings [66]:

No builder (soap alone)	86.6
Sodium bicarbonate	80.7
Modified soda	80.7
Soda ash	80.7
Metasilicate pentahydrate	79.3
Trisodium phosphate–12 H_2O	79.2
Caustic soda	78.0

A mixture of 80% potash cocoa soap and 20% of a silicate ($K_2O \cdot 3.3\ SiO_2$) prevented deposition of ferric oxide as well as soap alone, and better than with raw umber [37]. The order for ferric oxide deposition prevention was soap mixture > silicate > potassium hydroxide or potassium carbonate. With umber the potassium hydroxide and carbonate were generally poorer.

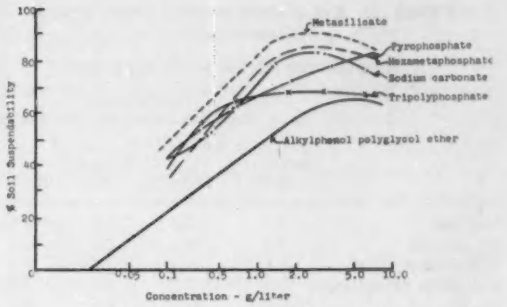

Fig. 8. Soil suspendability [60].

Weatherburn and coworkers [76] evaluated laurate, oleate, and stearate soda soaps with ten builders using standard Micronex C carbon as a soil. Without soap the suspending power remained low, and the initially high effect was reduced with increasing builder content. Two exceptions to this generalization were sodium chloride and sodium hexametaphosphate, and the latter actually increased the suspending power of sodium oleate. When the suspending power was plotted against the pH value of the combination, three categories were found: simple electrolytes, silicates, and phosphates. In these classes the best silicate was the meta compound, while hexametaphosphate was the best in its class.

Combinations of 60% dodecylbenzene sodium sulfonate with 40% builders were evaluated for soil prevention against raw umber and ilmenite [37]. With the exception of the sodium sulfate mixtures, both the $Na_2O \cdot 2.1\ SiO_2$ and sodium metasilicate combinations with the surfactant were improvements over the surfactant alone. Improvement in preventing deposition by added builder [60] was found to be least (negligible) with dodecylbenzene sulfonate, slight to moderate with cetyl sulfate, and markedly effective with alkylphenol polyglycol ether. Each set of curves exhibited optimum combinations:

Dodecylbenzene sulfonate 1 part to 2 parts builder
Cetyl sulfate 1 part to 2 parts builder
Nonionic 1 part to 1 part builder

Figure 8 demonstrates the general type of curves obtained.

Table X shows the relatively specific effect of builder upon surfactant in preventing deposition.

TABLE X. Redeposition with Surfactant–Builder Mixtures [47]

(Values indicate relative fabric brightness)

	Surfactants			
	Na Sulforicinate	Teepol	Igepon T	Na Laurate
NaCMC	2.5	15.8	8.0	5.9
Na silicate	2.7	8.1	1.5	8.9
Tripolyphosphate	8.5	5.6	2.0	4.8
Trisodium phosphate	2.6	15.2	7.0	3.8
Na_2SO_4	8.5	6.7	8.9	6.2

In summarizing the soil suspension data (redeposition values) the following are salient points.

In general, alkaline builders increase soil deposition, apparently as a sodium ion effect: best of the builders are silicates and phosphates, showing some protective action.

Surfactants, even those not forming insoluble salts in hard water, are enhanced in redeposition prevention when calcium ion suppressing agents are used with them.

As a class, nonionic surfactants are outstanding in preventing carbon soil deposition.

For soap–builder mixtures, three categories of builders were found: simple electrolytes, silicates, and phosphates. Most effective were the latter two, particularly sodium metasilicate and sodium polyphosphate.

Redeposition Preventive Agents

Relatively small proportions of certain agents to surfactants can cause very considerable increases in redeposition prevention, thus warranting critical review of their suggested mechanisms of action. Sodium carboxymethyl cellulose (NaCMC), one of the outstanding agents, has been the subject of enough published information to permit an extensive treatment of the subject. Consequently, references will be selected with the objectives of briefly reviewing evaluation data and of discussing the mechanisms involved in their application to the general picture of redeposition prevention.

Sodium Carboxymethyl Cellulose Evaluation Data

Considerable investigative work has been reported [62, 67, 68, 69] showing marked improvement in the soil preventive characteristics provided by NaCMC in compositions comprising soda ash and other builders with dodecylbenzene sulfonate and nonionic detergents. This work is characterized by the relatively high NaCMC levels recommended. In all cases, improvement in preventing soil redeposition was demonstrated. Stüpel [60] demonstrated that dodecylbenzene sulfonate effectiveness in preventing soil redeposition could be improved by adding NaCMC, the improvement increasing with increase in the NaCMC added.

Armstrong et al. [1] tested ten surfactants alone and with 1% and 10% of NaCMC added. Except for a cationic surfactant, all showed improved resistance to soil redeposition, the higher percentage providing at best only slight improvement over the lower concentration level. Wagg [74] demonstrated that the addition of NaCMC to sodium carbonate-surfactant mixtures reduced but did not completely prevent redeposition. Vitale [71] showed that NaCMC added to builder-surfactant mixtures could prevent neutral salts from causing soil deposition.

Improvement in whiteness retention (by adding NaCMC to the detergent composition) of repeatedly washed garments was shown over a period of time. A NaCMC pretreated fabric versus an untreated control when washed 16 cycles (in the absence of NaCMC addition) showed persistence of whiteness retention for the pretreated garment [25].

Bayley and Weatherburn [4] investigated the effect of added NaCMC on soap–builder compositions, their results in general being summarized in Figure 9. The greatest improvement from NaCMC addition is shown in those cases where the most marked reduction by builder addition had occurred; e.g., sodium carbonate, showing greatest increase in redeposition, was improved most by NaCMC usage. Table X shows that the redeposition preventive effect is somewhat dependent upon the surfactant.

Electrolytes, particularly those with polyvalent cations, result in a lowering of redeposition prevention. NaCMC is claimed to inhibit redeposition in the presence of mono- and polyvalent cations [49]. Soaps for example, remove divalent cations by precipitation, and deposition resulting from the concomitant sodium ion or salt effect is small. Redeposition is increased in the presence of electrolytes such as sodium chloride or sodium sulfate, and the adverse effect of small amounts can be overcome by adding NaCMC [10] or by removing them from the composition altogether [71]. Sodium carbonate

adversely affects redeposition prevention, even when added to surfactant solutions, but its effect can be minimized or overcome through the judicious addition of NaCMC [74]. It is interesting that the sodium carbonate effect does not seem to occur with nonionic surfactants.

Sequestering agents such as the tetrasodium salt of ethylenediaminetetraacetic acid (EDTA) and sodium tripoly phosphate, which react stoichiometrically with the ions causing water hardness, are also effective redeposition preventives. They are characterized by maxima in their whiteness retention curves, followed by a lowering in effectiveness attributed to the increased sodium ion effect [49].

Soil redeposition prevention may be affected by temperature change. In general, an increase in temperature of solutions containing NaCMC is said to lower whiteness retention, and the same is said to be true for non-NaCMC containing compositions, but to a lesser degree [69]. Other investigators [10] demonstrated that soap shows a large negative temperature coefficient of suspending power and claimed enhanced suspension power for NaCMC-containing compositions at either low or high washing temperatures. The suspending power of both Igepon T and dodecylbenzene sulfonate compositions containing NaCMC was greatly enhanced at either low or high wash temperature.

In general, when the initial suspending power of the detergent solution is high, NaCMC has little effect. However, when this power is low, resulting from builder usage, the addition of NaCMC in the correct proportion promotes better whiteness retention. The greatest improvement through NaCMC action is evident in those cases where suspending power has been reduced most through builder usage [4].

Adsorption

In the absence of available data it might logically be assumed that the effectiveness of surface active NaCMC could be attributed to adsorption, either as a protective film on the fiber substrate or as a more effectively dispersed, less adherent NaCMC–soil complex.

One proponent of the NaCMC–fiber school demonstrated this by painting a solution of NaCMC on cotton, rinsing, then soiling with India ink [35]. The presence of soil resistant areas in the treated surfaces seemed to confirm this view. However, oily soil on the fiber surface prior to NaCMC treatment tended to inhibit the soil preventive effect. The effectiveness of NaCMC for cellulosic fibers was explained on the basis that its crystal structure was so similar to that of cellulose that adaptation to the crystal lattice of the fiber occurred [24, 35]. However, inspection of fiber surfaces by electron micrography was unsuccessful in showing NaCMC adsorption [52].

The fact that fabrics repeatedly washed in NaCMC-containing detergents did not become grey or yellow as rapidly when NaCMC was withdrawn was taken as a further indication of adsorption in some manner. The fact that NaCMC is not effective with other fibers seemed to indicate preferential sorption at the cotton fiber interface [14].

Bartholomé and Buschmann [3] by adsorption experiments seemed to show preferential sorption of NaCMC, but Stawitz [54] by using radioactive

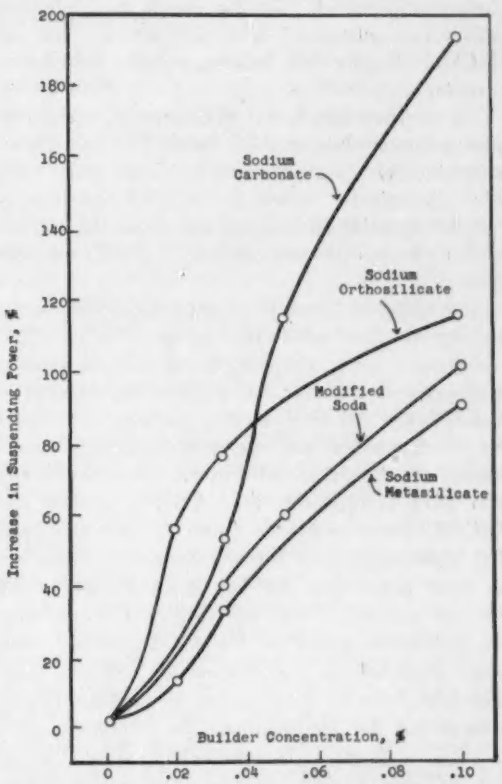

Fig. 9. Increase in the suspending power of built soap solutions due to the addition of 0.005% NaCMC [4].

tagged NaCMC was able to show that their data were incorrect because no correction for hydration of the cotton fiber had been made. A variation of the adsorption explanation [41] is that insoluble calcium and magnesium salts of NaCMC, formed in the hard water wash liquors, are very slowly desorbed with resultant retained redeposition prevention.

The radiotracer technique [54, 56] showed that 10γ of NaCMC were retained per gram of cellulose, in an occluded state, and that any NaCMC in excess of this easily migrated to the fiber surface in the water during the drying operation, a further indication of lack of adsorption. Similar results were obtained with acetate rayon, perlon, and wool fibers, further strengthening the occlusion theory.

Another adsorption technique was attempted [33], in which already sorbed partially sulfonated alkylarylpolyglycol ether on cotton fiber was subjected to an aqueous solution of NaCMC; no displacement of the surfactant occurred. Similar results were obtained with surfactant-treated bentonite particles, nor did NaCMC displace alkylsulfonate from polystyrene particles.

The presence of alkaline builders with surfactants increased the adsorption of NaCMC 13- to 25-fold from the 10γ per gram of cotton basis [55]. Another investigator found a 50–120% increase in NaCMC sorption on Vinylon and rayon staple fibers by the addition of surfactants to NaCMC solutions [26].

Adsorption of NaCMC on the soil particles rather than on the fiber substrate was indicated by Stüpel and Rohrer [61], using a fluorescence microscopy technique. A soil–NaCMC complex appeared to be formed when Acridine orange was used as a tracer dye, while no NaCMC appeared to have been deposited on the fiber. However, Nieuwenhuis and Ton [41] pointed out that Acridine orange and NaCMC form complexes (even precipitates), and that these aggregates formed on soil particles are no clear proof that NaCMC itself interacts with the soil particle. Nor did they believe that the soil preventive action of NaCMC-containing solutions depended on the interaction. Actual wash tests performed in the presence of Acridine orange showed that the dye destroyed the protective action of either soap or soda ash builder alone. When NaCMC and Acridine orange were used together, the protective action was lower than with the dye alone, suggesting that the NaCMC–Acridine orange complex bound soil to the unbleached cotton.

In an attempt to explain apparent differences, Nieuwenhuis and Ton [41] secured the fibers and materials used by Stüpel in his fluorescence microscopy work and those used in the radiotracer work of Stawitz and coworkers [33, 55, 56]. The unbleached yellow cotton used in the radiotracer work could have retained waxes and was almost certainly different in character from bleached white cotton used in other work. Madsen [35] had already noted the reduction in affinity of the carbon in NaCMC when fatty substances were present on the fiber. In a series of experiments the solvent extracted unbleached fiber and the bleached fiber were washed in a soil system containing as surfactant the partially sulfonated alkylarylpolyglycol ether in the presence or absence of NaCMC. The graying of the unbleached cotton was the same either in the presence or absence of NaCMC, while with bleached cotton under the same conditions the protective action of NaCMC was very evident.

Comparison with Nonionogenic Agents

Fong and Ward [14] investigated polyvinylpyrollidone (PVP) and polyvinyl alcohol (PVA) as soil redeposition preventives. There is ample evidence that PVP is adsorbed to an appreciable extent by carbon soil, and that the extent of this adsorption is halved by the presence of added detergent. This suggests that PVP adsorption may be competitive with surfactant on carbon black for adsorption sites, or may be due to a molar interaction between PVP and the surfactant, reducing PVP activity. There is no indication of a similar degree of PVP adsorption at the fiber substrate surface.

A sharp difference between NaCMC and the nonionogenic additives is the effectiveness of the latter on wool as well as cotton, further indicating activity at the soil rather than the fiber interface.

Electrokinetic Effects

Stillo and Kolat [57] postulated that ionogenic additives such as NaCMC function primarily by increasing the electrokinetic repulsive force as a result of being adsorbed on soil and/or fiber. Nonionogenic additives such as PVP were assumed to function through adsorption on the substrates, but to lower the nonelectrical attractive forces or increase the

nonelectrical repulsive forces. A decrease in nonelectrical attractive forces was attributed to an increase in the minimum permitted distance of approach of soil to fabric, while the other was attributed to a decrease in the configurational entropy resulting from the deposition of soil; in either case the function of the additive was said to be steric in nature.

The electronegative surface charge on cotton was increased by NaCMC [14], and this effect was said probably to be due to the presence of carboxy groups in this compound [40]. This suggests that redeposition prevention may be related to an electrokinetic repulsive force between fabric and soil. Nonionogenic additives cannot act from such a mechanism, since they show no such effect on the surface charge of either the soil or fiber.

Electrophoretic measurements [14] showed that in a tripolyphosphate–sodium carbonate–dodecylbenzene sulfonate composition none of the additives such as NaCMC, PVA, or PVP had appreciable effect on the surface electrical charge of the carbon used as the test soil. It was concluded that stabilization of dispersed soil as a result of electrokinetic effects was not a limiting factor in antiredeposition value.

Other Mechanisms

Increase (improvement) in the micelle forming characteristics of surfactants by NaCMC was suggested as one mechanism of NaCMC action [67].

An apparent correlation seemed to exist between deflocculation of soil and redeposition prevention [14].

Said to be partially responsible for NaCMC effectiveness are protective film formation and water solubility of the deposited film [24].

Sedimentation results showed that PVP had no significant influence on the degree of carbon dispersion. Action of PVP, because of adsorption by soil, was related to its effect on nonelectrokinetic forces of the van der Waals' type between soil and fiber [14].

Increased solvation associated with the lyophilic character of PVP could contribute to its antiredeposition properties. It was suggested that adsorption of NaCMC by the soil may result in a unique increase in hydration of carbon particles [14].

As an alternative to adsorption, it has been suggested that NaCMC may be mechanically held in fiber interstices, or may be held by hydrogen bonding [55]. A mechanical entrainment of cotton and/or carbon particles by a NaCMC network was suggested as not being impossible [41].

Two views [49, 68] seem to exist concerning sequestering and water softening action of NaCMC by comparison with the stoichiometric action of tetrasodium ethylenediaminetetraacetate and sodium tripolyphosphate.

Possible Mechanisms of Suspending Action

The suspending action of surfactants in preventing soil deposition on substrates has been investigated extensively under such diverse terms as soil redeposition, whiteness retention, prevention of soil deposition or redeposition, and so on. Suspending action as discussed occurs in relatively complicated dynamic systems, seemingly minimizing the value of data obtained by measurements under static conditions.

Forces Involved

Soil redeposition results from the existent opposing attractive and repulsive forces operative in detergent systems. Repulsive forces may be of the electrical double layer interaction type, and a relatively very short range type may also be active. Repulsive forces due to nonelectric interaction of the surface adsorption layers of particles are also possible [11, 57]. Attractive forces are mechanical entrapment, electrostatic, and sorptive in character. The latter are said to be particularly important, as these London-van der Waals' forces are universally active [11, 57].

The characteristics of a soil–fiber system (certainly with chopped fiber) may be considered as largely colloidal in view of the relative particle sizes and the large irregularities and areas of the surfaces involved. With this basic understanding, soil redeposition may be considered as equivalent to coagulation of a colloidal dispersion, and colloid stability theory may apply [57].

During laundering, two mechanisms are said to be in operation [10]: (1) distribution of suspended soil between the liquor adhering to or interpenetrating the fabric and the remainder of the detergent bath and (2) attachment of soil particles to the fiber surfaces. In the first mechanism, surfactants are said to do little to reduce redeposition, because it is necessary to establish equivalent concentration gradients in colloidal systems. There is some evidence

that NaCMC when adsorbed on soil particles can reduce or prevent diffusion of small soil particles into finer capillaries of the fiber or fabric structure, but this is said not to be an important factor with most fabrics.

Considerable thought and experiment have been expended on the effect of mechanical forces on soil entrapment, removal, and redeposition. Some investigators consider mechanical soil entrapment one of the main forces involved in the soil deposition mechanism.

If oil-free soil were bound to the fiber only by mechanical entrapment, true detergent solutions should readily be more effective than water in removal of this soil from the fiber; as this does not occur, a further explanation other than mechanical entrapment alone must be sought [9, 46].

The application of a small quantity of energy in the form of mechanical agitation to soil–fiber complexes resulted in relatively large decreases in soil retention by the fiber [21]. It was pointed out that detachment of soil particles by agitation results in a soil-exchanging process, essentially a type of equilibrium in the system [19]. The relative stability of soil–surfactant, soil–fiber complexes under mechanical agitation is a function of the energy applied and the compositional characteristics of the complexes dependent upon relative concentrations of the components. The formation of a soil–fiber complex is said to be a rate process [19] dependent upon the probability of close approach of soil particle to a site on the fiber surface in which it can be permanently occluded. Soil particles are weakly occluded in acceptor sites whose geometric relationship to size and shape of the particles renders them easily removable. Temporary blockage of acceptor sites has a marked effect upon soil deposition, which is dependent upon agitation severity. The effect of degree of agitation on deposition in the presence of sodium oleate, for example, is important; at low agitation there is little effect on deposition, but at higher energy levels the probability of permanent soil deposition was reduced, the lowering of adhesional forces becoming of increasing importance [43].

In the prevention of deposition by NaCMC it was said not to be impossible that the lattice or network structure of its solutions could mechanically entrap cotton and/or soil particles [41], but unless more than usual concentrations of NaCMC were used, this suggestion would appear unlikely.

Adsorption

At least a portion of the effectiveness of surfactants (detergents) may be attributed to their ability to align themselves at interfaces; this tendency to orientation results in adsorption at the surfaces (interfaces) involved.

Simple sorptive bonding of soils probably is almost universal in soiled garments, and it has been shown that it is the grease layer which further bonds carbon soil to cotton fiber surfaces, the bonding becoming more predominant as water is removed from the grease–carbon–cotton system [20]. As all fibers possess a normal moisture content, maintenance of a film of water of hydration could readily prevent soil particles (or grease) from approaching to within the attractive distances for more secure bonding (adsorption). As soil particles less than a micron in diameter are approached, the London-van der Waals' forces can become effective [52]. Broadly speaking, the principal role of surfactants in preventing soil deposition results from their ability to reduce the probability of soil attachment to fiber surfaces [10], but they would seem to be effective in a much more specific manner. It is characteristic that adsorption by van der Waals' forces leads to equilibrium and is reversible, while adsorption by chemical bonding occurs in stoichiometric proportions and is irreversible [54]; it is the former which generally operates in surfactant solutions (the latter represent stains). Whiteness retention is closely related to sorption of ions or molecules from solution by fabric and soil and suggests reduction in the van der Waals' attractive forces [14].

Hydrophobic soils are prevented from deposition by build-up of adsorbed films [46] which result in changes of adhesional energies. The charges which hydrophobic soils acquire through the preferential sorption of ions from solution are characterized by this adsorption, attributed to ion-induced dipole interaction; that is, an ion near the surface induces a dipole in the surface molecules, and attractive forces result. Anions, because of their higher polarizability and lower hydration, are more readily adsorbed than cations. This is particularly true of OH ions, due to the formation of hydrogen bonds which are strong dipole interactions, as well as to the unsymmetrical structure of the ion [57].

A suggestion that a complete monolayer of adsorbed surfactant is necessary to give a stable soil dispersion apparently is untrue. It was shown

that maximum protective action of sodium dodecyl sulfate was reached considerably before enough of the surfactant had been adsorbed to form a monolayer. This action was explained on the basis of the stabilization of aggregates rather than of individual particles [72]. Suspending action is attributed in part to the electrostatic repulsion of the particles on which adsorbed ionized surfactants are present and to the nature of the exposed surfaces, particularly in higher concentrations of the surfactants and in all concentrations of nonionizing surfactants [76]. Adsorption of both ionizing and nonionizing redeposition preventives on soil and/or substrate is indicated as at least one factor involved in their effectiveness [57]. Borrowing from nonaqueous media involving carbon as the suspendate, molecules of surfactant adsorbed by the carbon have been found to prevent these particles from approaching to such short distances as to enter each other's sphere of attraction [65].

The amount of carbon deposited from detergent solution seems to bear no simple relation to the amount of surfactant (sodium dodecyl sulfate) adsorbed either by the carbon or the cotton substrate; the adsorption of surfactant continues a uniform increase over the concentration range in which the amount of carbon deposited first decreases, then increases with increasing surfactant concentration [72]. The surfactant concentration at which deposition decreased very slowly with surfactant increase was much lower than the critical concentration (cmc) and seemed to vary directly with the concentration of carbon in the suspension [42].

It was suggested [65] that the surface areas of carbon blacks are probably densely set with polar C–O bonds and with other polar groups, owing to the presence of ash-forming constituents. Hence these dipoles attract polar or highly polarizable molecules. An explanation for the effectiveness of nonionic surfactants [46] suggests that carbon sorbs these nonionics with the polar groups in solution; hence to compress the polar groups would require an entropy decrease (which does not readily occur), with the result that the particles with adsorbed coatings are prevented from approaching closely enough for the attractive van der Waals' forces to become effective.

Sedimentation

Application of Stokes' law to the gegenions attached to soil particles 1 μ in diameter indicated that such gegenions did not account for suspending action. In dynamic systems, suspending power is concerned not with sedimentation (static conditions) but with the likelihood of collision and adhesion between the soil particles and substrate [43]. No direct relationship seems evident between suspending power and redeposition prevention [14], but sedimentation and deflocculation effects can be interrelated.

Deflocculation

Disaggregation of particles of soil to approach their individual particle condition can affect redeposition values. Decreases in sedimentation values (ultracentrifuge) were interpreted as partial disaggregation of particle clusters, charged additives producing further decreases in the order of molecular charge of the suspendate [14].

The rate of soil deposited where agglomeration is minimized was said to increase as the carbon particle size distribution was changed to give higher percentages of small particles, and to increase as the initial particle size of the carbon dispersion was decreased [19]. Doubt was cast on these conclusions because reflectance values were used, which are not necessarily a quantitative measure of actual soil deposited. At any rate, the presence of surfactants was found to decrease the rate of soil deposition.

Though early work [7] suggested that deflocculation was inadequate for explanation of antiredeposition values, more definite work [46] contradicts this conclusion, and deflocculation was indicated as the controlling factor in preventing soil redeposition.

If micro-occlusion of soil particles were more important than adsorption, then the average size of carbon aggregates in suspension from which deposition occurred would play an important role, since smaller particles would more easily penetrate the small roughnesses of the fiber. In a definitive experiment, the average aggregate size was shown to vary greatly with surfactant concentration to become markedly smaller, but at this point no marked change in carbon deposition was found. It was concluded that no direct relationship existed between degree of dispersion and aggregate size distribution in suspension [72].

A logical explanation for redeposition prevention in view of the effectiveness of nonionic surfactants for carbon soil is a deflocculation mechanism [46].

Soil Particle Size

The effect of particle size upon reflectance measurements is quite important. Considerable effort has been expended to demonstrate conformity of reflectance readings to quantitative soil deposition and, with exceptions, reflectance values do not parallel actual quantities of soil deposited.

Electron micrographs of fibers soiled with carbon black of small particle size did not support the view that macro-occlusion on the fiber surface was the dominant mechanism of soil retention [52].

A comparison of reflectance with radiotracer data [23] highlights the importance of soil particle size in redeposition measurement; extremely fine size particles generally resulted in more apparent soil deposition. Earlier investigators by reflectance methods had already shown the sharp increase in reflectance as a critically small particle size was reached [20]. Reflectance values were lower for a given quantity of carbon, the more finely divided was the dispersion [42]. The work of Compton and Hart [21] was said to show only that smaller particles of soil gave lower reflectances, not that more particles of soil were present [46]. Other work seems to support the theoretical conclusion that the tendency of particles to deposit on fiber increases with decreasing particle size [52]. The average particle size of a soil suspension can be decreased by adding strong stabilizing agents, but it was pointed out that this leads to a greater decrease in fabric reflectance for a given weight of soil deposited [10].

Small particles initially removed can be redeposited on fiber by virtue of their instability [11], this generally occurring in systems low in additives of any kind. Importance of particle size to measurement is indicated in the fact that carbon particles of 30–50 mμ lack the stability of very small particles and obscure other phenomena. It was suggested that soil particles 1 μ or greater in diameter are mechanically trapped and would be removed comparatively easily, as compared with smaller particles subject to sorptive forces [52].

The formation of soil–fiber complexes was said to depend on soil particle size [9]; an apparent straight-line relationship, which suggested [16] stoichiometric reaction between soil and surfactant with nonparticipation of cotton as a function of mass action, must be incorrect, since soil particles were involved, not molecules [46].

Solvation

It has been suggested that the effectiveness of NaCMC in preventing soil deposition may be attributed to hydrogen bonding of the fiber–NaCMC complex [55], or that a unique increase in hydration of the carbon particle results from NaCMC usage [14].

Simple sorption, solvation, or hydration can be important to subsequent results, and cotton (a polar fiber), which can sorb as much as 60% of its own weight of water, can affect the apparent degree of adsorption of surfactants [54]. It is very likely that the degree of hydration (hydrophobicity) of a fiber can have considerable effect upon soil redeposition. Under the same experimental conditions, soil redeposition has been shown to vary widely between cotton, silk, wool, linen, nylon, or Fortisan. Similarly, the suspending powers of different surfactants for the various fibers also vary widely [21], undoubtedly due to fiber adsorption characteristics (polarity).

Miscellaneous

The presence of calcium and magnesium in water causes increases in soil deposition, even with surfactants which do not form insoluble salts with these ions. Materials which sequester calcium and magnesium ions generally are effective in aiding in the prevention of soil deposition.

Concerning surfactants, combinations produce effects said generally to be nonlinear and nonadditive [10]. Soap is said to possess a peculiar self-protecting action against hard water effects [71], undoubtedly by softening water and reducing the calcium and magnesium ion effects. Acid soaps, which are more strongly adsorbed than unhydrolyzed soaps and have higher protective action, are unfavorably affected by the addition of alkaline salts [43].

Wetting action is said not to be a prime factor in redeposition prevention [10].

Summary

Soil suspension tests in the presence of substrate are superior to those made in its absence, but at the expense of increased complexity of the system. Among factors mentioned as affecting the soil–substrate relationship are mechanical, chemical, and electrical forces affecting both soil and substrate; adsorption of surfactant (or antiredeposition agent) on

substrate and/or soil; sedimentation; deflocculation; soil particle size; solvation; and several of lesser potential.

Surfactants are enhanced in soil deposition prevention by added builders such as polyphosphates and silicates, particularly when calcium ion is suppressed. Outstanding in preventing carbon soil deposition are nonionic surfactants.

Interpretation of mechanisms proposed for the action of sodium carboxymethyl cellulose in preventing deposition indicates probable action by adsorption on the cellulose substrate. Data of equal persuasiveness for similar action by surfactants are lacking.

Precise measurement of deposited soil has been difficult by reflectance methods; use of radiotracer tagged soils, only recently begun in this field, promises aid in elucidating the soil suspension mechanism.

Considering the complexity of these dynamic detergent systems, it is not surprising that a clear mechanism has not yet been advanced to explain soil suspension during the cleaning operation.

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A Simple Ballooning Yarn Apparatus

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Abstract

In order to demonstrate certain properties of a ballooning yarn, an inexpensive and easily constructed apparatus has been made, which has proved very useful for experimental and teaching purposes. The apparatus can be used for quantitative measurements of yarn tension, particularly with multiple balloons. A bibliography of ballooning theory is appended.

Introduction

The balloon of yarn which the human eye sees when a length of yarn is whirled around a package is an everyday occurrence in spinning and winding. On ring and cap spinning and doubling machines, on uptwisting machines, and whenever yarn is withdrawn at speed overend from a stationary package as in winding and warping, various types of yarn balloon are encountered which have certain common features. The shape of these balloons and the tension of the yarn forming the balloon affect both machine design and operating conditions, and have been the subject of a number of theoretical studies and investigations which, for convenience, have been listed at the end of this paper. To illustrate ballooning theory and to demonstrate balloon properties on processing machinery usually requires sensitive and often expensive equipment, which is not always available for ordinary teaching purposes, and a need seemed to exist for some device to simulate the more important features of yarn balloons in a form suitable for classroom experiments and demonstrations. In an attempt to fulfill this need, the apparatus described below was designed.

Description of Apparatus

The ballooning apparatus is little more than a miniature mechanized "skipping rope." The rope or yarn is held between synchronously rotating centers, one of which is attached to a balance to determine the yarn tension. Gregory et al. [9] have described equipment for the accurate study of balloon characteristics of lengths of yarn, both ends of which are positively rotated, the whole apparatus being enclosable in an air-tight chamber for use with low atmospheric pressures. The apparatus shown in Figure 1 is much simpler, as it is not intended for refined work or for use with fine yarns. Only the lower end of the yarn is positively rotated, the other end being turned by the torque provided by the horizontal component of the yarn tension at the apex. Goshawk [7] has mentioned an even simpler method of balloon formation under fixed tension conditions.

Referring to Figure 1, a small variable-speed fractional horsepower motor m, having a maximum speed of 8000 r.p.m., drives, by means of a band passing round pulleys p_m and p_s, an aluminum disc D mounted on a steel shaft running in ball bearings. There are a number of small holes spaced at uniform intervals along a diameter of disc D, through one of which the lower end of the yarn is attached, the upper end passing through a small hole O in the short spindle S. This spindle is free to rotate in a miniature ball bearing, the outer race of which is attached to the housing B. A spindle E, having stirrup R attached to it, is fixed to the center of housing B, so that the spindle can slide vertically through holes hh, being prevented from rotating by the stirrup contacting the frame F. Spindle E and the parts attached to it are supported by an inextensible thread Y which is attached to a scale pan P after passing around ball bearing pulleys bb.

The weight of the scale pan is arranged to balance the weight of the whole spindle assembly E plus the vertical frictional force at holes hh, so that the vertical component of the yarn tension at the apex O can be indicated by placing weights in the scale pan just sufficient to cause the stirrup R to contact

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the surface U of the fixed frame with zero force. The total balloon height is adjusted by raising or lowering frame F.

Determination of Balloon Shape

By suitable choice of background and lighting, a very clear image of the yarn balloon can be obtained, from which direct measurements may be taken. Alternatively, balloon dimensions can be determined from a photograph. Figure 2 shows a typical four-fold balloon, on which the botton driving disc, part of the top support, and the scale pan are visible. Figures 3 and 4 are flash photographs of the same four-fold balloon and show two views of the individual yarn line taken simultaneously by cameras situated at right angles to each other.

Apparatus Limitations

The apparatus is unsuitable for use with fine yarns and for very narrow balloons, when the horizontal component of the yarn tension at O is insufficient to provide the very small torque necessary to rotate spindle S. Equally, the apparatus is unsuitable for use with yarns whose thickness is appreciably affected by twist. This is because when starting from rest, the angular velocity of spindle S does not immediately equal that of disc D, and during this brief period of acceleration twist is inserted into the yarn. However, during normal running, stroboscopic observations of the spindle and the disc have shown perfect synchronization of the rotation of the ends of the yarn, so that after this initial period, no further twisting occurs. It is obvious that the apparatus cannot simulate axial yarn movement due to winding on or off a package, so that the Coriolis effect is absent. During spinning with normal yarn twist this is unimportant, but the effect cannot be ignored in balloons formed when the linear yarn speed is considerable, as occurs during low twist spinning.

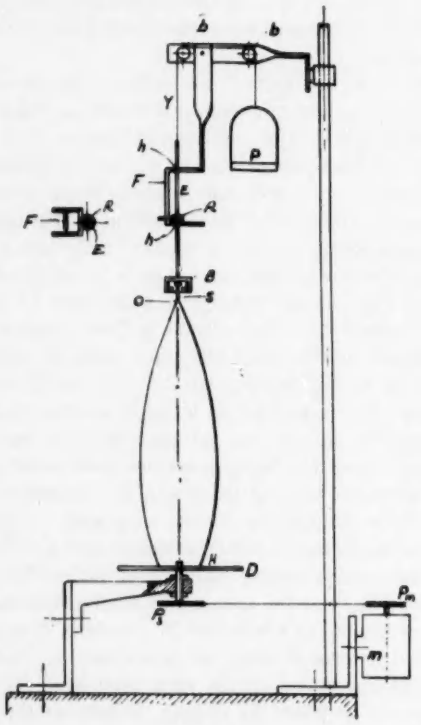

Fig. 1

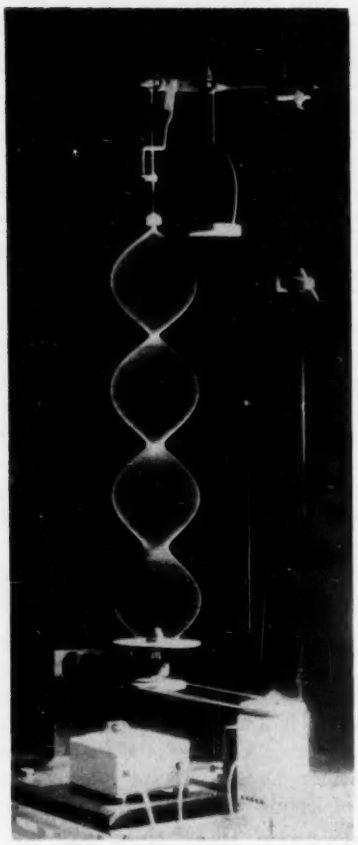

Fig. 2

during uptwisting, and during overend withdrawal on winding machines.

The accuracy of the tension measurement depends upon the free vertical movement of spindle E passing through holes hh. These parts must be carefully constructed and lubricated so as to be virtually friction free.

Some Applications

The equation numbers in this section refer to those of Grishin [12] derived for yarn balloons where the Coriolis force, gravitational force, and yarn rigidity can be ignored. The equations have been slightly modified in order to express yarn count in tex units.

With reference to the diameter of a multiple balloon such as Figure 2, each of the minima is termed a "neck" and each of the maxima a "bulge."

In all the experiments described below, the yarn used was a lightly waxed 12-ply linen thread of 182 tex resultant count.

Balloon Height and Yarn Tension

The relationship between the balloon height and the vertical component of the yarn tension given by the apparatus with single balloons is indicated by the graph of Figure 5. For these experiments the length of yarn forming the balloon was adjusted to ensure that all balloons had a constant bulge diameter of 17 cm., balloon base diameter and speed being constant at 4.45 cm. and 5700 r.p.m. respectively. This shows good agreement with Grishin's Equation 32, which can be written:

$$T = \frac{0.112\, n^2 H^2 N}{10^3 (cH)^2}$$

where T = vertical component of yarn tension (g.), n = balloon rotational speed (1000 r.p.m.), H = loop height (cm.), and N = yarn count (tex). The quantity cH is given by Equation 28:

$$cH = \pi - \text{arc sin}\, \frac{D}{\delta_m}$$

where D = base diameter (cm.) and δ_m = bulge diameter (cm.). Equation 32 becomes $T = 0.08\, H^2$ in this example; the graph of Figure 5 shows this parabola.

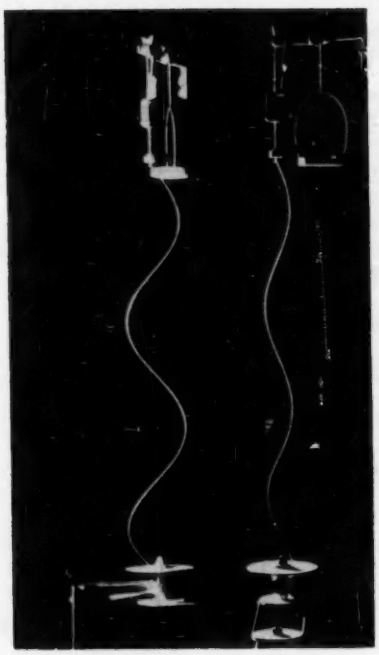

Fig. 3 Fig. 4

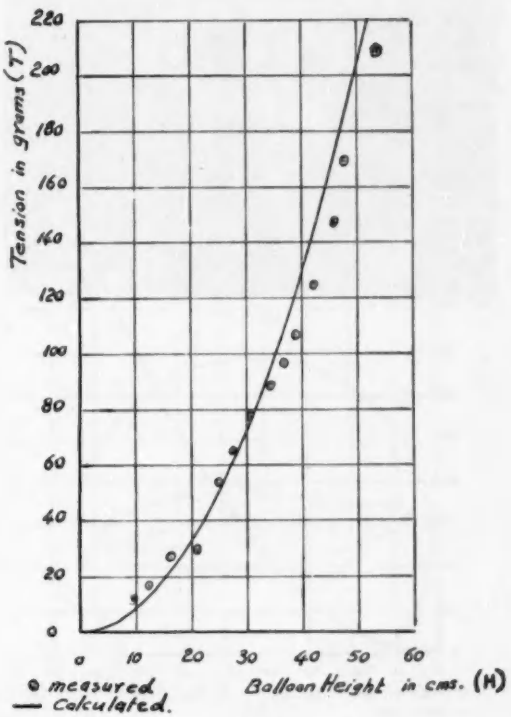

Fig. 5

In a second series of experiments keeping a constant length of yarn between the rotating centers of the apparatus, a stable six-fold balloon was produced, the tension and the diameter of the bottom bulge being determined. The total balloon height was then increased to give stable conditions with 5, 4, 3, 2, and single balloons successively, the same measurements being taken. These results are shown in Table I, the other balloon particulars being:

Length of yarn forming balloon: 99 cm.
Base diameter: 3.175 cm.
Balloon speed: 5200 r.p.m.

To ensure that the only parameter affecting the tension shall be the individual balloon height, it is necessary to adjust the measured tension values given in the table so that they correspond to a constant bulge diameter. By use of Equation 28, the value of cH corresponding to a bulge diameter of 9 cm., $(cH)_9$, is calculated, together with the value $(cH)_m$, corresponding to the measured bulge diameters, so that

$$\text{Adjusted tension} = \text{measured tension} \times \frac{(cH)_m^2}{(cH)_9^2}$$

The adjusted tension values are given in the table and are plotted on the graph of Figure 6, where the curve is the parabola $T = 0.0713\ h^2$, h being the average individual balloon height. This equation is actually that for a single balloon having a 9-cm. bulge diameter. In applying the equation in this manner, it is assumed that the individual balloon height h of the multiple balloon can be taken to be equivalent to the height H of a single balloon. Theoretically, the inaccuracy of doing this increases with the number of individual balloons. However, even for the six-fold balloon, the equation gives a very close estimate of the tension, and it is not considered that more accurate calculations of the tension (using values of cH from Equation 29) are worthwhile in this instance.

From Figure 6 the interesting conclusion can be drawn that the tension approximately varies in-

TABLE I. Yarn Tension With Multiple Balloons

Number of balloons, L	6	5	4	3	2	1
Total balloon height, H, cm.	77.0	79.0	84.0	88.2	90.7	93.0
Average height, $h = \frac{H}{L}$	12.8	15.8	21.0	29.4	45.4	93.0
Bulge diameter of first balloon, cm.	7.2	8.0	8.5	9.2	10.0	15.0
Measured tension, g.	10	14	27	52	124	490
Tension adjusted to 9-cm. bulge diameter, g.	9.3	13.4	26.5	52.0	125.5	517.0

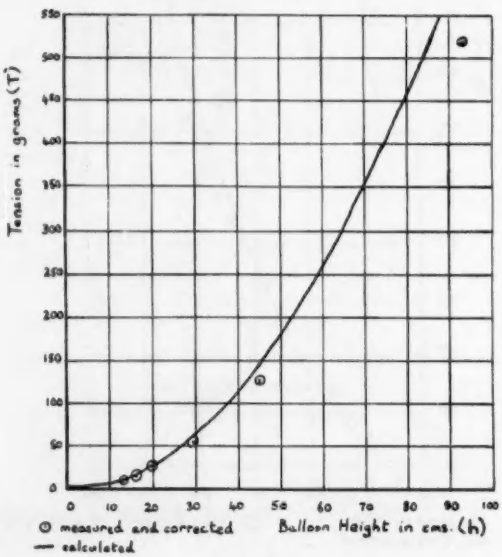

Fig. 6

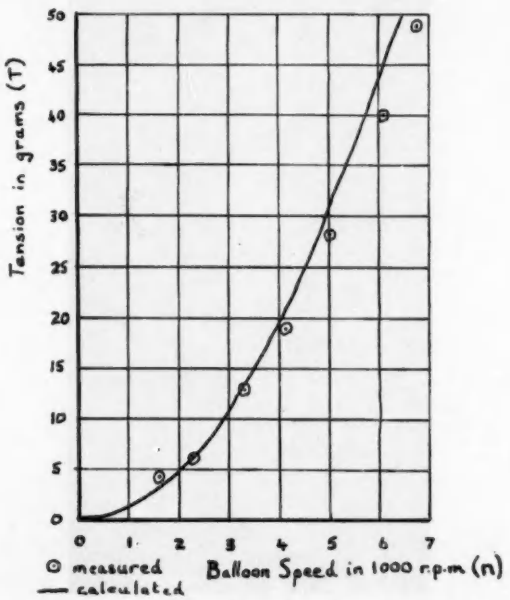

Fig. 7

versely as the square of the number of balloons, for multiple balloons where the total height can be adjusted to form various numbers of individual balloons with the same maximum bulge diameters.

Balloon Speed and Yarn Tension

When a stable yarn balloon is obtained, the effect of changes of speed of rotation on the balloon shape is only slight. The graph of Figure 7 shows the relationship between the vertical component of yarn tension and balloon speed for a triple balloon where no measurable change in balloon dimensions was observed with changes in speed. The balloon particulars were:

Total balloon height: 63.5 cm.
Base diameter: 4.45 cm.
Bulge diameter of first balloon: 11.5 cm.

For these values, Equation 32 becomes $T = 1.214\ n^2$, the curve being indicated by the unbroken line of the graph in Figure 7.

Balloon Shape and Dimensions

The approximately sinusoidal path of the yarn forming a multiple balloon can be seen in the flash photographs, Figures 3 and 4. The yarn path does not pass through the axis of rotation except at the balloon apex, and thus the necks visible in Figure 2 are formed. The increase in neck diameter towards the base is very pronounced.

While the path of the yarn projected onto a plane normal to the balloon axis can be obtained from two path projections on planes at right angles to each other passing through the axis, such as Figures 3 and 4, it is interesting to obtain a direct flash photograph, such as Figure 8a. It can be seen that difficulty was experienced in obtaining sufficient depth of focus, and the yarn path has been redrawn in Figure 8b, where H is the lower end and O the apex. Figure 8a shows a similar though not identical four-fold balloon to Figure 3 and 4.

The occurrence of necks rather than nodes (when the yarn path passes by the balloon axis) is due to air resistance. Values of the balloon diameter are given in Equation 22.

$$\delta_x = D \sqrt{\frac{\sin^2 cx + (ax)^2}{\sin^2 cH + (aH)^2}}$$

where δ_x = balloon diameter at distance x below the apex, D = balloon base diameter when $x = H$, a = air drag parameter, and c = centrifugal force parameter. In vacuum, when $a = 0$, the equation becomes:

$$\delta_x = D \frac{\sin cx}{\sin cH}$$

This represents the classical Lindner [15] equation when the yarn path passes through the balloon axis, forming true nodes.

Under normal conditions when $a > 0$, the numerator in Equation 22 must exceed zero except when $x = 0$, and thus $\delta_x > 0$ except at the balloon apex. Necks occur when $\sin cx = 0$, so that if the height of each balloon is the same, the neck diameters will increase in the ratio 1:2:3: . . . n corresponding to the 1st, 2nd, 3rd . . . nth necks (numbering from

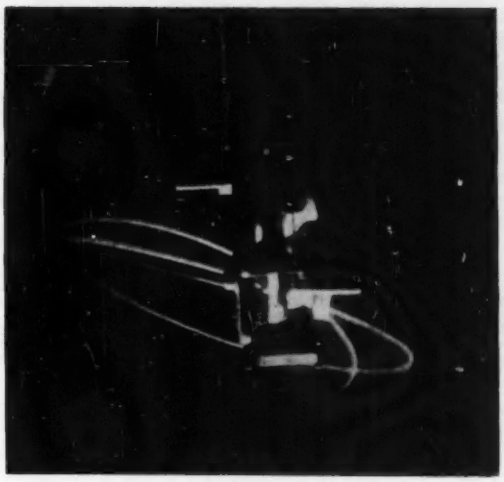

Fig. 8a

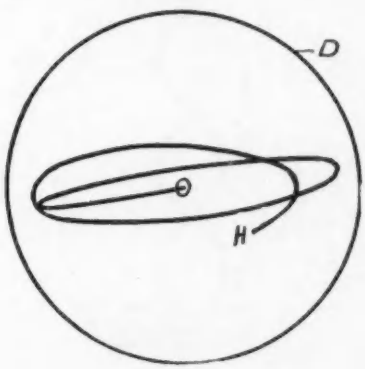

Fig. 8b

the apex downwards). Bulge diameters increase at a very much smaller rate.

Figure 9 is a dimensioned drawing of the profile of a four-fold balloon where the broken line shows the actual shape and the unbroken line the shape calculated from Equation 22, using Equation 10 to obtain the air drag parameter. The experimental particulars were:

Length of yarn forming balloon: 74 cm.
Base diameter, D: 4.45 cm.
Balloon speed, n: 5850 r.p.m.
Balloon height, H: 56 cm.
Measured tension, T: 15 g.
Bulge diameter of first balloon: 10.4 cm.

The measured and calculated values of the positions of the bulges and necks are in good agreement, as are the ratios of the neck diameters and of the bulge diameters, but the calculated diameters underestimate the measured values by 13%. The discrepancies are attributed to differences in the air drag characteristics of the ply linen yarn used for the experiments compared with those of singles cotton yarns for which Equation 10 was intended.

Ballooning Theory Bibliography

The literature dealing with theoretical aspects of yarn ballooning has increased considerably during the last seven years or so. While not attempting a rigorous discussion of the simplifying assumptions and methods of calculation adopted by different authors in considering various aspects of yarn ballooning, this descriptive survey may be of some convenience to teachers and others interested in the use of the simple ballooning apparatus.

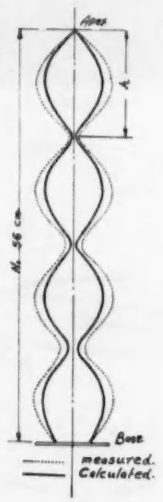

Fig. 9

While not the first to consider the shape of a ballooning yarn on the ring spinning frame, in 1910 Lindner [15] derived a simple equation (see above) for the yarn tension in a narrow balloon considering only the centrifugal forces on the portion of yarn forming the balloon. In 1934 Grishin published work on the same problem, taking into account both air drag on the yarn and the Coriolis forces due to the linear yarn velocity with reference to balloons formed on ring spinning frames [10] and during unwinding overend from stationary packages [11]. Most of this work has been summarized and extended further in book form [12], the equations having direct application in instances such as those encountered with the ballooning apparatus.

With particular reference to worsted cap spinning, where Coriolis forces can be neglected, Hannah [13, 14] explained the behavior of relatively narrow yarn balloons, enabling new shapes of cap to be designed, reducing yarn tension variations during spinning. A somewhat similar problem was considered by Mack [16] for ring and cap spinning, making more exact assumptions for air drag. Development of this work showed that with double balloons the neck diameter could be used as a measure of air drag [17], while with the sophisticated ballooning yarn apparatus already mentioned [9], practical confirmation of Mack's theory was possible [8]. Mack and Smart [18] have more recently considered the different though associated problem of the radius of the free end of a length of yarn trailing from a rotating bobbin.

Considering yarn balloons on continuous filament ring and cap spinning machines where, due to the low amount of twist inserted in the yarn, relatively high linear yarn speeds are encountered, Crank [3] allowed for both air drag and Coriolis forces on balloons where the maximum diameter is up to 50% of the balloon height (i.e., on both narrow and broad balloons). This work was extended for different cap [4] and ring [5] spinning machine conditions.

Bracewell and Greenhalgh [1, 2] were concerned with the use of balloon control rings on long-lift ring frames, finding that if the yarn path is assumed to lie along a catenary, sufficient accuracy can be

obtained to enable machine operating conditions to be determined. De Barr [6] considered the yarn balloon on a cotton ring frame as part of a stationary wave system of circularly polarized transverse vibrations on a stretched string, in order to explain balloon characteristics. The special problem of ballooning during unwinding overend from stationary packages has been dealt with by D. G. Padfield [19] for cylindrical packages and single balloons. Similar equations to those of Mack [16] have been used, with the addition of the Coriolis terms, which are of particular importance in this application. This work has recently been extended to cover multiple balloons [20].

It is interesting to note that no work particularly directed to the circumstances of yarn ballooning during uptwisting appears to have been published.

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* Copies of these papers can be seen at the libraries of T. M. M. (Research) Ltd., Helmshore, Rossendale, Lancashire, England and the Manchester College of Science and Technology.

INDUSTRIAL SECTION

Formic Acid Colloid of Methylolmelamine as a Weather and Rot Resistant Finish for Cotton[1]

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Abstract

A study of application techniques of methylolmelamine resins to cotton has revealed a practical method for producing cotton fabric with outstanding rot resistance and improved weather resistance. This method is based upon the use of an acid colloid of methylolmelamine. The method of application of the colloid is the same as that conventionally used for resin finishing; that is, pad, dry, and cure. The main difference is the use of formic acid to produce a colloid. Photomicrographs show that methylolmelamine colloids (1–4 hr. old) are deposited in the outer portion of the cell wall of the fiber, whereas the conventional process deposits resin about halfway through the cell wall and the wet-cure Arigal [3] process deposits uniformly throughout the cell wall. Colloids five hours or older are deposited in much the same position as obtained by the conventional process. Only the fresh (1–4 hr.) colloids give outstanding rot resistance.

Cotton fabric finished with the acid colloids compares favorably with partially acetylated, fully acetylated, cyanoethylated, and Arigal fabrics which are known to have excellent resistance to rot. Experimental evidence indicates that the mechanism through which rot resistance is acquired by the acid colloid is "controlled penetration" rather than a continuous surface film.

Several acids were evaluated for colloid production; formic was the only acid which produced suitable colloids. A number of metal halides have been used as catalysts with the colloids. Small amounts of the metals become tenaciously bound in the fabric, and some of the metals alter outdoor weathering and other properties of the fabric.

Introduction

A study of application techniques of methylolmelamine resins to cotton has revealed a practical method for producing cotton fabric with rot and weather resistance. In previous work with melamine-formaldehyde resin, Nute [8] reported its use in treating cotton insect netting for the armed services to provide shrinkage control in combination with water repellence and mildew resistance. The studies of White and Siu [12] demonstrated that resin impregnated cotton fabrics were resistant to microbiological deterioration when subjected to pure culture mildew tests and two-week soil burial tests. Investigations by Cooke [3] of the resistance of resin-treated cellulosic fabrics to microbial attack at add-ons of 15–20% resin showed little or no loss in strength after burial in a potent soil burial bed for six weeks. In the same experiments it was found that fabric treated with 1% by weight of an aqueous dispersion of copper-8-quinolinolate completely disintegrated when exposed for six weeks in the soil

[1] Presented at the Chemical Finishing Conference of the National Cotton Council, Washington, D. C., October 1, 1958.

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[3] Use of a company and/or product named by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

bed. In all of the above work, the melamine formaldehyde and other aminoplast resins were applied by the conventional process. By conventional process is meant the application of an aqueous system of a resin former and a latent acid catalyst to a textile followed by a dry and a cure at elevated temperatures.

Another method of using aminoplasts for protection of cellulosic fibrous material from attack by microorganisms has been reported in a patent by Ruperti [11] and assigned to Ciba Limited. This method is now known as the Arigal[3] process. According to the patent, the main difference in this treatment and the conventional method of application is that the monomer is cured in the presence of water at a temperature not to exceed about 80° C. This is usually accomplished by the use of steam. The time required for curing by this process is generally more than one hour, which is rather inconvenient for many American finishing plants.

The use of aminoplast resins as weather protective finishes has been reported by several investigators [2, 4, 5]. Although the resin add-ons used were approximately 5%, they did afford good protection to cotton fabrics.

The object of the present paper is to present a process for using an acid colloid of methylolmelamine to impart rot and weather resistance to cotton fabric. The method of application of the colloid is essentially the same as that conventionally used for resin finishing; that is, pad, dry, and cure. The main difference is the use of formic acid in the treating solution to produce a colloid. The term acid colloid as used in this paper refers to methylolmelamine molecules and polymers of trimethylolmelamine which are associated and stabilized by polar acid groups. All of these materials possess light scattering properties.

Acid colloids of aminoplast resin formers have been used before, but not to impart rot resistance. Numerous investigators [10, 13] have shown that a remarkable improvement in the wet strength of paper is obtained with colloidal solutions. The colloids reported by the earlier investigators were significantly different from the colloids we have found useful, even though the starting materials were the same. In the earlier studies the colloids were permitted to age, often as much as 24 hr., thus allowing rather large polymers or colloidal particles to form; these materials coated the cellulosic fibers, causing them to stick together; in this way textiles were stiffened and paper was given increased wet strength.

Acid colloid impregnated cotton fabrics have been shown by Nute [9] to be unique textile finishing materials in producing excellent shrinkage control and durable stiffness, with no loss in tensile strength. Here again, the colloids were allowed to age at least 24 hr. before use. These large colloid particles were deposited on the surface of the fiber. Cooke [3] observed that a cotton fabric impregnated with an aged acid colloid of methylolmelamine completely deteriorated when exposed to a two-week soil burial test. This was a much shorter deterioration time than that observed when the resin was applied by the conventional method.

Materials and Methods

Fabric Description

The cotton material used was a bleached 80×80 print cloth weighing approximately 3.12 oz./sq. yd. The print cloth was processed in commercial continuous peroxide bleaching equipment.

Chemicals Used

All of the N-methylol compounds used were commercial products sold under various trade names. The compounds were trimethylolmelamine (Resloom HP; Aerotex Resin UM Special), methylated trimethylolmelamine (Aerotex Resin M-3), dimethylol urea (Aerotex Cream 450), either type of dimethylol urea (Aerotex Resin 801), and dimethylol cyclic ethylene urea (Rhonite R-I). Formic and acetic acid were commercially available products.

Processing Procedure

In each case the textile finishing agent (resin-forming monomer) was first dissolved in water; then the acid was added. In some cases the solutions were used immediately; in other cases, where indicated, the solutions were allowed to stand one or more hours after the acid was added before it was used. Where metal halides or an alkanolamine hydrochloride (Catalyst AC) were used as latent catalysts, a concentration of 1.75% catalyst (solids content) based on the weight of the resin was incorporated in the finishing solutions immediately after the addition of the acid. Samples of print cloth were impregnated on a laboratory padder, dried 4 min. at 80° C., and cured for the same length

of time at 140° C. in a forced draft oven. The samples were washed in hot running water for 15 min. to remove unreacted resin and air dried.

Test Methods

The following properties were determined by the usual ASTM procedures: breaking strength, strip method [1a] (except the strips were raveled to 80 threads); crease resistance, Monsanto method [1e]; resistance to flat abrasion, inflated diaphragm method, rubbed multidirectionally [1c]; flex abrasion [1d]; soil burial [1b]; and tear resistance, Elmendorf method [1f].

For convenience all breaking strength results are reported as percentages of the materials as first exposed, unless otherwise stated.

Weather exposure tests were conducted in New Orleans, Louisiana, in an unshaded location, with the samples exposed on open-backed wooden racks facing south at an angle of 45° from the vertical and at a minimum distance of 30 in. above the ground.

Results and Discussion

Treatment of Print Cloth with Trimethylolmelamine, Metal Salts, and Acetic Acid

In the past few years, the use of metal salts as the catalyst for N-methylol finishing agents has been increasing. Analyses of resin treated cotton have shown that small amounts of the metals (about 0.2%) are tenaciously bound in the fiber. Since some metals are fungicidal, it was felt that the mildew and rot resistance of finished fabric might be improved by merely using the appropriate metal halide as the catalyst. When resin forming solutions of trimethylolmelamine were made up, it was found that some metal halides could be added directly to the solutions in the same manner as the commercially used $MgCl_2$ and $Zn(NO_3)_2$ catalysts. But it was found that the addition of $FeCl_3$ and $CrCl_3$ resulted in the precipitation of basic salts when the metallic chlorides were added to the trimethylolmelamine solutions, which are initially slightly alkaline. These two salts could be kept in solution when the treating solutions were slightly acidic. Therefore, the metal salts were used under two sets of conditions: (1) metal salts other than iron and chromium were added to the slightly alkaline solutions of trimethylolmelamine or (2) trimethylolmelamine solutions were acidified with acetic acid (2.3% based upon the total weight of the solution) and then metal salts were added. All of the metal salts studied were stable in the acidified solutions. For comparative purposes one solution contained an alkanolamine hydrochloride as catalyst and one contained acetic acid as the only catalyst.

The finishing solutions were made up to contain 17% trimethylolmelamine and used immediately on 80 × 80 print cloth. The metal salts and alkanolamine hydrochloride were used in the solutions to the extent of 1.75% based upon the weight of the trimethylolmelamine. The fabric was padded, dried, cured, rinsed, and air dried. The dry was for 4 min. at 80° C. and the cure was 4 min. at 140° C. The finished fabrics contained 12% resin add-on except the one which contained only acetic acid as the catalyst, and this fabric contained about 9% resin.

The percent strength retained by the methylolmelamine treated fabrics after exposure for various periods of soil burial is shown in Table I.

As can be seen, fabrics containing 12% resin applied by the conventional process using conventional catalysts or other metal salt as latent catalyst were practically deteriorated after six weeks of soil burial. These results compare favorably with the data reported by Cooke [3]. However, the fabrics treated with either the acid colloid solution (acidified with acetic) or with the acid colloid containing a metal salt retained 100% strength for the same period of exposure. The fabrics treated with colloids containing chromium and iron chlorides had strength retentions of 94% and 90%, respectively, even after 18 weeks of soil burial.

From an analysis of Table I, it seemed quite likely that the improved rot resistance resulted from the addition of acids to the trimethylolmelamine solutions because, in all cases where the metal salts were employed in both basic and acidic systems, the improved rot resistance was obtained only in the presence of the acid. Also, the most outstanding rot resistance was obtained when $FeCl_3$ and $CrCl_3$ were added to the acetic acid solutions. This corresponds to the fact that aqueous solutions of these two metal chlorides are more acidic than the other metal salts used. Therefore, the solutions containing $FeCl_3$ and $CrCl_3$ in addition to acetic acid were the most acidic solutions.

As mentioned above, it is known that aminoplast resins applied by the conventional technique are ef-

fective in retarding the degradation of cotton by weather. Previous studies conducted on the aged acid colloid of methylolmelamine had not included any weather exposure evaluations. Therefore, it was thought profitable to evaluate fabric finished with an acid colloid. Table II gives the results obtained on the fabrics described above after eight months of weather exposure. It can be seen that the acid colloid treated samples (samples treated with solutions which contained acetic acid) retained as much strength as the samples treated by the conventional methods, and all are better than the untreated print cloth. One exception should be noted: the sample treated with the acid colloid and using $FeCl_3$ as the catalyst had about the same percent strength retention as the untreated control.

TABLE I. Rot Resistance of Print Cloth Treated with Trimethylolmelamine, Metal Salts, and Acetic Acid

Catalyst used, 12% resin add-on	Strength retained after soil burial, %				
	2 wk.	4 wk.	6 wk.	12 wk.	15 wk.
Catalyst AC	91	33	19	—	—
Catalyst AC plus 2.3% acetic acid	100	100	95	65	24
Catalyst MX	52	13	3	—	—
Catalyst MX plus 2.3% acetic acid	100	100	100	59	30
Catalyst $Zn(NO_3)_2$	95	49	24	—	—
Catalyst $Zn(NO_3)_2$ plus 2.3% acetic acid	100	100	100	47	26
Catalyst $MnCl_2$	50	12	10	—	—
Catalyst $MnCl_2$ plus 2.3% acetic acid	100	100	96	60	29
Catalyst $NiCl_2$	71	30	11	—	—
Catalyst $NiCl_2$ plus 2.3% acetic acid	100	100	100	66	38
Catalyst $CoCl_2$	94	25	23	—	—
Catalyst $CoCl_2$ plus 2.3% acetic acid	100	100	100	83	47
Catalyst $CuCl_2$	100	27	16	—	—
Catalyst $CuCl_2$ plus 2.3% acetic acid	100	100	100	59	35
2.3% Acetic acid*	100	100	56	20	—
				9 wk.	18 wk.
Catalyst $CrCl_3$ plus 2.3% acetic acid	100	100	100	100	94
Catalyst $FeCl_3$ plus 2.3% acetic acid	100	100	100	100	90

* Resin add-on of 8–10%.

TABLE II. Weather Resistance of Print Cloth Treated with Trimethylolmelamine Metal Salts, and Acetic Acid

Catalyst used, 12% resin add-on	Strength retained after outdoor exposure, %			
	2 mo.	4 mo.	6 mo.	8 mo.
Catalyst AC	100	100	100	100
Catalyst AC plus 2.3% acetic acid	100	100	100	94
Catalyst MX	100	100	94	92
Catalyst MX plus 2.3% acetic acid	100	100	100	100
Catalyst $Zn(NO_3)_2$	98	98	92	76
Catalyst $Zn(NO_3)_2$ plus 2.3% acetic acid	100	100	100	98
Catalyst $MnCl_2$	100	100	100	95
Catalyst $MnCl_2$ plus 2.3% acetic acid	100	100	100	100
Catalyst $NiCl_2$	100	100	100	91
Catalyst $NiCl_2$ plus 2.3% acetic acid	100	99	98	90
Catalyst $CoCl_2$	100	100	93	86
Catalyst $CoCl_2$ plus 2.3% acetic acid	100	100	100	100
Catalyst $CuCl_2$	100	84	84	72
Catalyst $CuCl_2$ plus 2.3% acetic acid	100	92	92	82
Catalyst $CrCl_3$ plus 2.3% acetic acid	100	100	99	91
Catalyst $FeCl_3$ plus 2.3% acetic acid	84	77	67	56
Acetic acid—2.3%*	99	98	94	69
Untreated	82	62	61	54

* Resin add-on of 8–10%.

TABLE III. Rot Resistance of Print Cloth Finished with Formic Acid Colloids of Trimethylolmelamine

Age of colloid used, 12% resin in finished fabric	Strength retained after soil burial, %					
	2 wk.	4 wk.	6 wk.	12 wk.	18 wk.	21 wk.
Freshly prepared	100	100	100	100	100	100
2 Hr.	100	100	100	100	92	78
4 Hr.	100	100	100	63	21	—
5 Hr.	100	100	75	38	24	—
6 Hr.	100	100	76	21	7	—
7 Hr.	97	87	62	15	—	—

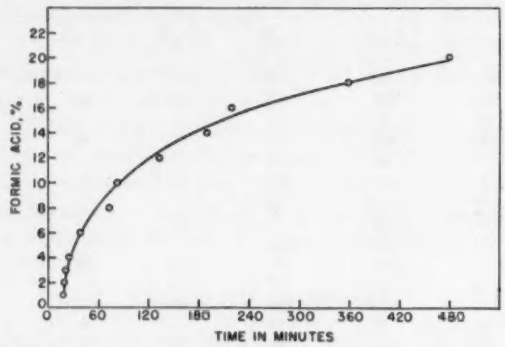

Fig. 1. Time of stability of the colloidal solutions with varying amounts of formic acid.

Preparation of Stable Formic Acid Colloids of Trimethylolmelamine

The methylolmelamine solutions described above, in which acetic acid and metal salts were incorporated, were stable for only brief periods. Generally, a precipitate began to form after the solutions had stood for about 30 min. This was true even if the amount of acetic acid was increased. With 7% or more of the acetic acid, precipitates formed immediately.

Since stable formic acid colloids of methylolmelamine had been reported in the literature [9], it seemed desirable to determine what amount of acid was necessary to produce a stable colloid and to determine if such a colloid could be used to impart the degree of rot resistance obtained with acetic acid and chromium and iron chlorides. If such a finish is to be practical in a textile finishing plant, the solution must be stable for longer periods of time than 30 min. Therefore, a series of solutions was made in which the methylolmelamine concentration was held constant at 17% while the amount of formic acid was varied up to 20% of the weight of the total solution. The time required for a precipitate to occur was noted.

Figure 1 gives the time of stability of the colloidal solutions, as judged by the appearance of a visible precipitate, with varying amounts of formic acid. The solution with 4% or less acid began to deposit a precipitate within 25 min., which was about comparable to that found with acetic acid. At these low concentrations, the formic acid acts primarily as a polymerization catalyst. Higher concentrations of formic acid have a stabilizing effect and also act as a polymerization catalyst. The colloid solutions containing 20% formic acid were stable for at least 8 hr., which would be suitable for practical applications. Obviously, the larger amounts of acid have a marked stabilizing effect on the colloid.

Finishing with Formic Acid Colloids of Trimethylolmelamine

Fabric samples were treated with solutions containing 17% methylolmelamine and 20% formic acid to explore the value of formic acid colloids and the effects of aging colloid solutions. Print cloth was impregnated immediately (within 10 min.) after preparing the colloidal solution, and then at 2, 4, 5, 6, and 7-hr. intervals. Table III shows the percent strength retentions of the different samples at the indicated periods of soil burial. The sample treated with the freshly prepared colloid solution retained 100% strength after 21 weeks of soil burial, and the fabric impregnated with the solution aged for 2 hr. had 78% strength retention for the same period of exposure. The rest of the fabrics showed a decreasing resistance as the colloid solution was allowed to age. These results demonstrate that freshly prepared acid colloid resin solutions (and those aged less than 2 hr.) impart to cotton fabrics excellent resistance to microbiological deterioration. The aged colloids offered much less resistance to microorganisms.

It should be remembered that the trimethylolmelamine solutions used above were undergoing polymerization during the aging. When the solutions were allowed to stand overnight, a clear gel resulted which soon became hard and brittle. The rate of polymerization during the first seven hours was followed by determining the viscosity periodically. Figure 2 shows the change in viscosity as a function of time. It would appear from the curve that the fresh colloid was an association of essentially monomeric

trimethylolmelamine, because the first viscosity reading was taken immediately after adding formic acid to the aqueous solution of trimethylolmelamine.

Microscopical Examination of Acid Colloid Finished Cotton

Microscopical observations were made on several fabrics treated with trimethylolmelamine, using the conventional method and the acid colloid technique. The resin was found mainly in the outer portion of the cell wall of the fibers when fabric was treated with fresh colloids and with colloids up to four hours old. The lack of thorough penetration of the monomeric acid colloid into the cell wall of the cotton fiber is not too surprising. McBain [6] states that colloidal particles do not penetrate sufficiently compact colloidal substances, of which cotton is an example.

Upon examination of the Arigal treated fabric, the fibers were found to be completely and uniformly penetrated by the resin. As stated earlier, in this process the resin is cured in the presence of water, which probably retards the migration of the resin to the outer wall of the cotton fiber.

Effects of Colloid Add-On Upon Rot Resistance of Treated Fabric

Since the above work had been confined to using 12% add-ons of the trimethylolmelamine resin, it seemed desirable to determine if lower concentrations of resin would afford similar rot resistance. Therefore, fabric was treated to contain from 3% to 12% resin add-on. For the 12% resin add-on, the fabric was treated with a solution containing 17% trimethylolmelamine and 20% formic acid. To get the lower resin add-ons, more dilute solutions of trimethylolmelamine were used, but the concentration of formic acid was held constant. For example, 3% resin add-on was obtained by using a solution containing 3.4% trimethylolmelamine and 20% formic acid.

Table IV gives the percent strength retained by samples treated with the various resin add-ons after the indicated periods of soil burial. The samples with 12% and 10% resin retained 100% and 69% strength respectively after 15 weeks exposure, while the sample containing 8% resin retained 3% after 15 weeks, and the sample with 5% resin retained only 6% after 4 weeks. The sample with 3% resin was completely deteriorated in 2 weeks of soil burial. The results show that excellent rot resistance was obtained when the cloth was treated with fresh acid colloid solutions so as to impart 10–12% resin add-on.

Acid Colloid Finish Compared to Other Finishes

It is well known that cotton chemically modified by acetylation and cyanoethylation will withstand soil burial tests for far longer periods than cotton treated with commonly used fungicides. The strength retentions of three chemically modified cottons—partially acetylated, fully acetylated, and cyanoethylated—Arigal treated, and acid colloid finished fabric after 21 weeks of soil burial are shown in Table V. The acid colloid finished fabric contained 12% resin add-on and was prepared from a fresh colloid solution containing 20% formic acid. As can be seen, all samples still retained 90–100% of their original strength. It should be pointed out that cot-

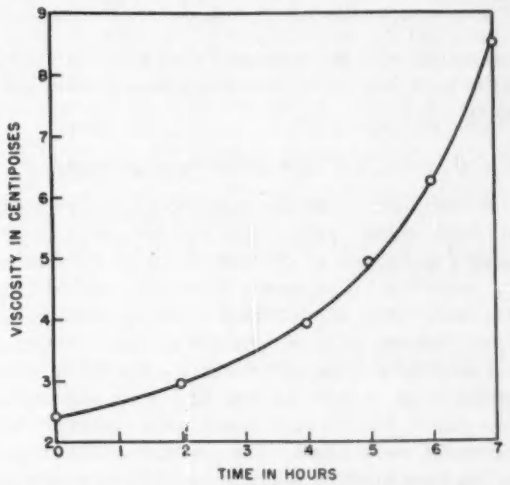

Fig. 2. Changes in viscosity of acid colloid upon standing.

TABLE IV. Influence of Add-On of Formic Acid Colloid Upon Degree of Rot Resistance

Resin add-on, %	Strength retained after soil burial, %					
	2 wk.	4 wk.	6 wk.	9 wk.	12 wk.	15 wk.
12	100	100	100	100	100	100
10	100	100	100	100	72	69
8	100	33	26	17	4	3
5	34	6	—	—	—	—
3	0	—	—	—	—	—

TABLE V. Rot Resistance of Print Cloth Finished with Trimethylolmelamine Acid Colloid and Other Finishes

Fabric finish	Strength retained after soil burial, %						
	3 wk.	6 wk.	9 wk.	12 wk.	15 wk.	18 wk.	21 wk.
Acid colloid, 12% resin add-on	100	100	100	100	100	100	100
Arigal treated	100	93	100	100	100	100	100
Partially acetylated, 22% acetyl	93	93	94	96	94	98	91
Fully acetylated, 35% acetyl	99	97	100	100	98	100	100
Cyanoethylated, 4.0% N	97	90	93	94	98	94	92

TABLE VI. Some Physical Properties of Acid Colloid Finished Print Cloth

Finish	Resin add-on, %	Breaking strength, warp, lb.	Elmendorf tear, warp, lb.	Stoll Abrader	
				Abrasion, flex	Wear cycles, flat
Acid colloid	12	32.53	1.04	87	94
Acid colloid	9	31.18	1.25	67	67
Acid colloid	7	33.44	1.32	96	96
Acid colloid	4	34.32	1.42	184	73
Acid colloid	2	35.14	1.60	499	85
Conventional	10	34.17	1.54	245	84
Untreated	—	41.94	2.07	734	91

ton treated with the commonly used fungicides normally loses 50% strength or more after 6 weeks soil burial.

Use of Acetic Acid with Other Resin Formers

Several other aminoplast resin formers were used to finish cotton print cloth by the conventional manner and by use of 2.3% acetic acid in the finishing solutions. The textile chemicals included in this study were a methylated trimethylolmelamine, dimethylolurea, an ether derivative of dimethylolurea, and dimethylol cyclic ethyleneurea. The fabric was treated so as to contain about 12% resin add-on in each case. The finished fabrics were evaluated by the use of the soil bed. The presence of the acetic acid in these finishing solutions had little or no effect upon the rot resistance of the fabric, as compared to the conventionally finished fabrics.

Some Physical Properties of Acid Colloid Finished Cloth

Several pieces of print cloth were finished with freshly prepared formic acid colloids of trimethylolmelamine to provide fabric for physical evaluation. The treating solutions contained 20% formic acid and sufficient trimethylolmelamine to give resin add-ons ranging from 12% to 2%. For comparative purposes, one piece of fabric was finished by the conventional technique using an alkanolamine hydrochloride as the catalyst; in this case the resin add-on was 10%. Table VI gives the test results obtained on the above fabrics and also on an untreated control fabric. The warp breaking strength of the colloid finished samples is the same as obtained for the conventional technique, all showing about 20–25% loss in strength compared to the untreated fabric. This loss is about normal for most resin finishes. The Elmendorf tear strength varied from 1.04 lb. to 1.60 lb. for the acid colloid samples, the higher values being for the lower resin add-on. The conventionally finished sample had a 1.54-lb. tear, while the untreated fabric had a 2.07-lb. tear value. The flex abrasion was reduced substantially by all the resin finishes; however, the flat abrasion tests showed no difference from the untreated fabric. The crease recovery angles for the colloid finished fabrics were quite encouraging. For example, the sample containing 7% resin had a recovery angle of 294 (W + F) compared to a value of 257 (W + F) for the cloth finished in the conventional manner. Investigations conducted by Nute [9] and Nuessle [7] showed that aged acid colloids do not impart crease resistance. The use of formic acid with various crease resistant finishes is being expanded and will be reported in the near future.

It should be pointed out that softeners were not used on any of the fabrics reported in Table VI. The use of an appropriate softener should increase noticeably the values found for tear and abrasion resistance.

Summary

Cotton fabric was made rot and weather resistant with trimethylolmelamine by addition of acetic acid and a metal salt to the aqueous solution of methylolmelamine just before finishing the fabric. The acidic solution had to be used immediately because insoluble

polymer began to precipitate about 30 min. after addition of the acid. The finishing process consisted of the usual pad, dry, and cure procedure.

Stable acid colloids of trimethylolmelamine were made by adding about 20% formic acid to the trimethylolmelamine solutions. The colloidal solutions were stable for at least eight hours. They were also applied to fabric by the pad, dry, and cure technique. When these colloidal solutions were used within about four hours after addition of the formic acid, the resin was deposited primarily in the outer portion of the cell wall of the cotton fiber. If the solutions were allowed to age for five to seven hours before treating fabric, the resin was found more deeply penetrated into the cell wall. However, according to prior work, when a similar colloid was applied to cotton fabric just before reaching the gel point, the resin coated the fiber.

Best rot resistance was obtained using the colloids within two hours after preparation. With 12% resin imparted by use of a fresh acid colloid, print cloth retained 100% strength after 21 weeks of soil burial. This is comparable to results obtained with partially acetylated, fully acetylated, and cyanoethylated print cloth and cloth finished by the Arigal process. The results were substantially better than those obtained with the same trimethylolmelamine applied by the conventional technique, and also much better than that reported for additive type fungicides. The extent or degree of rot resistance obtained with the acid colloid finish was dependent upon the use of a fresh acid colloid solution and upon the amount of resin put into the fabric. Best results were obtained by using acid colloids within two hours after preparation. About 10–12% resin add-on is needed in print cloth for good rot resistance.

The outdoor weathering characteristics of fabric was improved also by the acid colloid finish. However, this improvement was about equivalent to that obtained by trimethylolmelamine when applied by the usual or conventional technique.

The rot resistance imparted to cotton by acid colloids is accomplished by controlled penetration of essentially monomeric methylolmelamine, which subsequently is polymerized. Several experimental facts substantiate this statement. First of all, photomicrographs showed that fresh acid colloids penetrated only the outer portion of the cell wall. Secondly, the viscosity measurements showed that polymerization occurs slowly as the acid colloids are allowed to age. Therefore, only a very slight degree of polymerization has occurred within the first 2–3 hr. Additionally, experiments clearly showed that the most rot resistance was imparted with acid colloids which were used immediately after preparation.

Acknowledgments

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Study of Improvement of Smoothness of Cotton Fabrics[1]

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Abstract

An exploratory research has sought the most promising ways of imparting a high degree of durable smoothness to cotton cloth. This work, limited to laboratory procedures, has resulted in finishes characterized by different degrees of smoothness, of luster or glaze, and of durability. Smoothness was very well retained in the best of these finishes and can be considered permanent, although luster decreased gradually upon washing. Some of these finishes seem readily adaptable to lining and other apparel fabrics. The work was based on the use of an experimental calender and largely upon the calendering of cloth while it was wet, in a state of swelling greater than that from mere wetting with water. There would be difficulties in practical operation if the water in the cloth contained dissolved finishing agents or if the cloth was too wet. Objections have been partially met by preswelling, washing, padding the wet cloth in a softening and fixing agent, and then drying before calendering. Promising for further investigation is close control of moisture content of the cloth at the time of calendering, at levels between those of present practice and values attained in this research. A range of 15–40% regain in cottons treated as described, but only partially dried before calendering, is suggested. Higher calender temperatures and pressures should also be considered.

A STUDY of the improvement of smoothness of cotton fabrics has resulted in finishes of different degrees of smoothness, of luster or glaze, of durability, and a degree of novelty. While the purpose of the investigation was to find the most promising methods of imparting durable smoothness to cotton, luster has also been obtained almost unavoidably. This study consisted mainly of exploratory research toward the development of smooth finishes by chemical-mechanical means, with but little of the work primarily on luster. This research was made possible by the availability of an experimental calender at The Textile Research Center of the School of Textiles of North Carolina State College.

The possible field of research could not be nearly exhausted within the time allowable, and the work became mainly concerned with swelling cotton goods to make them more readily susceptible to mechanical deformation by calendering and with wet calendering of goods while in such a swollen state. While wet calendering has features which are, at least, undesirable, there were indications that such a process might be usable.

Earlier Processes

The most notable example of wet calendering is probably the process of Simili[4] mercerizing. According to an article on this subject [1], the process has been in use in Europe for more than 25 years. It consists in calendering ordinary wet cloth, or wet mercerized cloth, at 480–570° F. to obtain a durable or permanent luster.

It seems doubtful whether finishing agents such as resins or softeners should be added to cotton goods prior to wet calendering. However, according to a British patent [4], mercerized or unmercerized cot-

[1] A report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract was supervised by the Southern Regional Research Laboratory, Southern Utilization Research and Development Division, Agricultural Research Service. Presented at the Seventh Chemical Finishing Conference, National Cotton Council, Washington, D. C., October 1, 1958.

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[4] The use of trade names has been for information only, not as endorsement of a product of any firm over equivalent products of other firms.

ton piece goods can be padded with a resin solution to 70–80% wet pick-up and calendered at once to glaze or emboss the fabric.

There have been patents to cover pressing or calendering of wet mercerized cloth, notably cloth containing controlled amounts of caustic soda from incomplete washing after mercerizing [3], to obtain high luster.

The issuing of patents implies some basis for such methods as just mentioned, but familiar durable and permanent finishes are apparently produced by other methods. Such finishes involving resin and friction calendering may be subject to improvement, but their current success placed them outside the field of the present exploratory research.

So-called polished cotton of sateen construction, first seen since this work was begun, had an extreme permanent luster. It was not especially smooth according to its observed coefficient of friction, but it was smooth and soft in feel. It seems to meet the requirements of apparel fabrics contemplated in this research, but was made by methods which are believed to be familiar to finishers and were not followed up here.

Preswelling

The principle of a large share of the work being reported was simply to try by swelling to make the cotton as susceptible as possible to smoothing to a more nearly permanent form than ordinarily attained by calendering. This was done by preswelling the fabric, washing out the swelling agent, and calendering while the cloth was swollen to a much higher degree than by normal wetting. The preswollen cloth was in a state of transitory or residual swelling which would be largely lost upon drying.

Such a state of greater swelling under suitable conditions can be readily illustrated by mercerized cotton. When the two cottons are dyed together in the same bath, a sample of mercerized cotton that has not been dried will dye much darker than a sample which differs from the first only in having been dried before dyeing. In such a case, depth of dyeing is a rough measure of degree of swelling; the undried material was much more swollen in the dyebath than that dried and wet again in dyeing.

Somewhat more specifically, Coward and Spencer [2] reported that cotton treated with caustic of mercerizing strength, and thoroughly washed, retained about twice as much water when centrifuged as similar cotton swollen by water alone, due to great residual swelling.

There is similar residual swelling with sulfuric acid. Cotton swollen in acid of 63.4% concentration [7], thoroughly washed, and then centrifuged retained 128% of its weight of water. When dried and rewet before centrifuging, the same cotton retained only 57%, less than half as much, while cotton not preswollen, but thoroughly wetted and centrifuged, had only 50% retention. Such figures suggest that residual swelling effects might be utilized.

Material Used

The base fabric for the experiments on finishing was 80 × 80 print cloth of 3.1 oz./sq. yd., singed and bleached. Fabric designated as mercerized consisted of some of the same material mercerized in a finishing plant. The latter was not noticeably lustrous, but came to nearly twice the depth of shade when dyed in the same bath with the unmercerized cloth. These fabrics were considered sufficiently different to show any substantially different effect from the use of regular mercerized cloth instead of the usual unmercerized print cloth.

A few other fabrics gave about the same results in finishing as the usual print cloth. A special sateen responded somewhat better.

Caustic soda and sulfuric acid were usually of commercial grade. Reagent cupri-ethylene diamine (Cu-en) was used at first. Then larger amounts were prepared in accordance with Straus and Levy [9], except that the method was simplified.

The copper was precipitated as basic copper sulfate but not separated from the supernatant liquid. The sodium hydroxide was added to the resulting mixture to form cupric hydroxide. Then, again with no separation from the supernatant liquid, the cupric hydroxide was dissolved in it after the addition of the specified amount of ethylene diamine. Neutral salts formed in the reactions were still present, but the results in the treatment of cotton were the same as obtained with equivalent strengths of the purchased reagent as prepared for viscosity determinations.

Methods

Samples of fabric were immersed in solutions to preswell the cotton prior to calendering. Preswelling includes treatment of fabric in caustic of mer-

cerizing strength and washing for immediate use wet, in distinction from the use of cloth previously mercerized in the usual way and dried normally. However, regular mercerized cloth has also been preswollen in agents other than caustic soda. The cloth, usually preswollen in caustic soda, sulfuric acid, or Cu-en, has been thoroughly washed, neutralized, and washed, with one exception to be described.

Some of the preswollen and washed samples were calendered wet for "pure" finishes. Other samples, not dried, had finishing agents, particularly softeners and resins, padded on them and were then calendered wet. This was done in spite of the possibility for unevenness in padding such materials into wet goods. Finally, some samples were dried after preswelling and addition of finishing agents, and then calendered dry instead of wet.

Since it would not be feasible in practice to calender cloth containing large amounts of water, such as 70% from padding, most cloth to be calendered wet was squeezed in the calender (cold), used as a mangle or wringer. The usual pick-ups were then 30–50%.

Cloth samples for finishing have been about as large as could be dipped uniformly by hand into treating solutions, and about as small as could be calendered satisfactorily. Samples have been treated in loose form (slack) without tension or restraint on shrinking, but usually on stainless steel pin-frames to yield finished samples a little over one square foot in area. While the frames do not duplicate practical conditions, they do allow the study of treatments in solutions which would otherwise cause objectionable shrinkage.

The calender has rolls of 22-in. face, and samples calendered have been 14–18 in. wide. They have usually been short pieces which had two passes (one nip each) through the calender, between a cotton and a heated steel roll, without normal tension. Most samples were calendered twice on the same side of the cloth, but some once on each side. The usual temperature of the steel roll has been 400° F. and the usual pressure 1100 lb. per inch of nip. Questions as to wet cloth cooling the heated roll could not be answered because of the running of discontinuous small samples.

When required, samples were cured after calendering in accordance with the requirements of Zelan AP Paste, or other softening or resinous agents.

Evaluation of Finishes

Finishes are judged largely by appearance and feel or hand. Kaswell, in his review [6] published in 1953, reported that the measurement of factors entering into hand was very unsatisfactory, and this seems to remain true. Of the three important elements of hand, smoothness, stiffness, and softness, smoothness and stiffness were measured on a routine basis. Even though Kaswell reported that no measurement correlated with personal observation of smoothness, our most important property, measurements were made to aid in screening the processes; they were not depended upon for final opinions on the finishes.

Smoothness was measured as coefficient of friction with the Frictionmeter (Dreby). Such measurement in terms of friction between specimens of fabrics seems to be in general accordance with suggested uses of smooth fabrics for linings and slips, even though no correlation is known with practical performance. Coefficients of friction from 0.2 to 0.3 are considered to represent very smooth samples, and fabrics having such values were really glazed. Values from 0.3 to 0.5, sometimes obtained after a glaze finish had been broken, after washing, etc. seem rather high for smooth fabrics, but fabrics that showed such values were sometimes very soft and smooth in feel.

As an indication of the difficulties of evaluation, four lining fabrics of indefinite identification, not all cotton, differed greatly in coefficient of friction in the two directions in the piece, evidently owing to fabric construction. There were values as low as 0.26–0.30 in one direction, but 0.63–0.88 in the other. Fabrics that felt smooth could hardly be rated as very smooth according to the tests.

Softness has been inferred from feel and stiffness. The latter has been measured as drape stiffness with the Drape Flex Stiffness Tester. It is recognized that a cloth sample may bend easily but not be soft. This instrument was used only for screening and to give a general idea of results obtained.

Nearly all finished fabrics have been subjected to direct dyeing as a special test, even though finished cloth like most of the samples would not normally be dyed. Such dyeing tends to break down glaze finishes that result from the calendering and to give an idea of their relative durability. Also, the relative depth of shade indicates effects of the finishing treatment on the cloth. To bring these out most

conveniently, groups of samples as produced were dyed together with controls in the same bath.

While dyed with a nominal 2% of color, one dye lot might include highly swollen cottons which dye much darker than normal and other samples, treated with fixing agents which reduce the swelling or accessibility of cotton, that dye very light. The dyeing thus serves to some degree to help evaluate the process as well as the finish. Since calendered pieces usually look lighter in color on the face than on the back, measurements of dye or of color are of doubtful significance. Relative depths of shade have usually been judged visually, sometimes in comparison with standard dyed samples, and usually on the backs of the finished samples.

There has been no evaluation of luster by any method of measurement, partly because many of the samples have been colored to various depths with a direct fast blue 4GL, and partly because there are various gradations between two types of bright finishes characterized by glaze and luster respectively. The term glaze is used to describe finished fabrics which reflect a great deal of light from smooth, closed surfaces. The term luster is used when surfaces which reflect well do not look closed, but show the individual threads more, and the effect is of the type commonly associated with textiles such as mercerized cotton.

Shrinkage has been observed by the measurement of marked areas before and after processing. The print cloth (80 × 80) shrank about 8% in area upon wetting, and samples processed on frames have usually shrunk by about the same percentage. There would appear to be no particular problem with shrinking if practical processing is conducted at ordinary tensions and finished cloth is suitably tentered.

Processes of General Application

Much work has been done on details of the application of specific swelling agents to cotton cloth. Some of the other materials used and the process steps can be discussed as of more general application.

Softening

Softness is a factor in the feeling of smoothness, so softeners of most types were tried. Some softeners tended to detract from luster and were therefore not desirable even though they may have served their intended purpose. Finally, Zelan AP was selected for most attention, as it represents the durable type of water repellent which was found to be of outstanding interest as a softener. It contributed not only to softness and smoothness, but frequently to the preservation of luster when finishes produced by calendering with about 3% Zelan present were broken or deglazed as described below.

Zelan had one particular general effect if present in preswollen goods which were calendered wet and then cured. It caused dyeing to about a third lighter shade than on similar preswollen cloth calendered wet without the Zelan. Effects of the Zelan on smoothness and luster are durable, although not permanent.

In contrast to calendering wet with Zelan present, when there is risk of its coming off on calender rolls and being redeposited on the goods, preswollen fabrics containing Zelan have been dried and then calendered. While it might seem that the drying would merely "undo" the effects of preswelling, cloth so treated and deglazed yielded relatively smooth, soft, and sometimes lustrous finishes, to be described.

Setting of Finishes

It would seem that materials padded into cotton cloth while in a state of high residual swelling should be absorbed in some manner different from their absorption by ordinary wet cotton. That is, any agent so applied to help set or fix smooth or lustrous finishes should be not merely present, but present in some more favorable way than usual. Also, such agents should be most effective when present while the cloth is undergoing deformation by the calender and partial setting under its pressure and heat.

In spite of implications that wet cloth containing textile resins can be calendered, it was decided from numerous experiments with resins intended to aid in the fixation of finishes that this could not be done in a practical way. Even small amounts of resins tried with Zelan in goods to be calendered wet are of doubtful practicability. Also, since the use of resins in connection with calendering would lead into a field already well known to finishers, it was unnecessary to go further in that direction.

Experiments were also made on calendering wet with such setting agents present as formaldehyde, glutaraldehyde, and alpha hydroxy adipaldehyde, but they are subject to the same general objections. Further, these and related materials require such

strong acid catalysts as to be questionable from the point of view of long term attack on both steel and cotton calender rolls.

While efforts were being made to set the finish for smoothness and luster, other efforts were necessary to break it down to some extent to attain softness.

Breaking Calender Finishes

All goods calendered wet became well dried by this process and were glazed in appearance and stiff, although usually very smooth. The cloth as calendered was too stiff for the present purpose, and such stiff finishes were not evaluated for possible uses outside the scope of the present investigation.

For end uses requiring soft fabrics, the stiff glaze finishes had to be broken or deglazed and made less stiff. There was no equipment available especially for such a purpose, so deglazing was done by improvised methods. One method already mentioned was direct dyeing, usually at the boil for 45 min. Some samples were reduced to a pleasing texture and luster in this simple manner, while many others retained much of their glazed appearance and remained quite stiff. Observations of appearance after such dyeing proved to be misleading. Many finishes were not as durable when washed in an automatic washer as seemed to be predicted by the degree to which they withstood a boiling dyebath.

Calendered samples have been deglazed in two other ways, one apparently too mild and one probably too severe. The first of these methods was boiling in an open kettle for 30 min. in a solution of 0.1% Duponol RA and 0.1% sodium carbonate—a composition recommended for scouring goods treated with Zelan for water repellency. The other method was running in an automatic washer in a solution of the same composition with a load of cloth (1:17.5 of solution), for 10 min. at 140° F., with the usual rinses.

These methods tell something of the relative durability of the finishes. As further tests on durability, the samples were given washes with 0.1% soap and 0.02% available chlorine at 140° F., in a similar washer for 10 min., with the usual rinses.

Nature and Amount of Swelling

The general nature of the work and materials used having been described, a few details on the extent and nature of the swelling may be of interest before we come to specific results.

There is no actual measure for the amount of swelling, but samples of cloth treated in such agents as sodium hydroxide, strong sulfuric acid, or Cu-en solutions, then washed, remain swollen much more than ordinary wet cotton cloth. That there is such residual swelling which persists after squeezing-out in the calender is clearly shown by higher percentage of pick-up, or retention of water.

The experimental calender, operating at 1100 lb. per in. of nip at room temperature, usually squeezed the plain wet print cloth down to 29–32% retention on the air dry basis (about 40%, bone dry). Similar cotton swollen in sulfuric acid of 65% concentration showed a retention of 70%, or more than twice that of cotton swollen in water alone. The cotton washed free from sulfuric acid must remain very strongly swollen to hold so much more water than ordinary cloth under the high calender pressure. Such residual swelling, although of more practical interest at somewhat lower levels, surely suggests possibilities for unusual effects in calender finishing.

Residual swelling depends upon the concentration of the swelling agent; examples are shown as retentions of water in Table I. The retentions upon squeezing in the calender have not always been the same under conditions intended to be similar, but there have been the same relative levels for different swelling agents and the same trends upward with concentration. The values shown (vertically) in the table for each series of concentrations of either reagent resulted from squeezing-out all at the same calender setting. In experiments of most practical interest the retentions have been below 50%, on the air dry basis.

Any relationship between degree of residual swelling and finish attainable is not clear because lustrous finishes that could not be told apart by inspection, and could scarcely be distinguished by feel, have been obtained, for example, with 20% sodium hydroxide, 63% sulfuric acid, or 0.25 molar Cu-en. Whatever the original degree of swelling of the cotton by the copper solution, the residual swelling was much lower than that following swelling by either of the other agents, as indicated by retentions (Table I). Nor is the nature of the swelling by the different agents the same, even though similar results may have followed their use. Sodium hydroxide has the advantage that it does not tend to dissolve cotton

but, rather, swells it to some particular degree at a given concentration, where the action practically stops. On the other hand, either of the other two agents can form gels and disperse or dissolve cotton, so they may sometimes attack the fibers slightly. Hence, even after washing, there may be a tendency for the fibers to stick together due to superficial gel and the pressure of the calender. Apparently as a result, the sulfuric acid and Cu-en sometimes yield glaze finishes which do not break down or soften easily, although they may tend to retain smoothness better than softer finishes. Incidentally, the impression has also been gained that smoother finishes may result if the cotton has been slightly degraded, as by acid attack, before wet calendering. Other differences in the nature of the swelling are brought out below.

Squeezing the excess water from a preswollen sample apparently reduces its residual swelling, because it reduces its dyeing capacity somewhat.

TABLE I. Retention of Water by Cloth Squeezed in Calender

Nature or treatment of cloth (80 × 80)	Water retention, %	
Wet print cloth	29–32	
Wet mercerized cloth	31–33	
Cloth preswollen in:		
Cu-en, 0.25 *M*	34–37	
Sodium hydroxide	1st set	2nd set
0% (water only)	29.2	28.9
12	34.5	—
17	43	41
20	47	44.5
23	—	44.9
Sulfuric acid	1st set	2nd set
0% (water only)	30.4	29.9
62.2	43	—
62.6	—	40.8
62.9	—	43.3
63.2	49.6	—
63.55	—	46.1
64.2	53.3	—
65.3	70.8	—

Treatments with Sodium Hydroxide

Preswelling has been tried with sodium hydroxide through a wide range of concentrations, beginning with 8%. Cloth was immersed loose in solutions of the lower concentrations where shrinkage was relatively low, and recovery of area would not be difficult. Under such conditions there would not be prohibitive shrinkage in solutions up to about 12% concentration, but then it increased rapidly up to about 20% caustic strength. When the samples were calendered wet and the finish broken by dyeing, there was also increasing durable smoothness and luster up to about 20% concentration. Such change of properties with processing cannot be closely defined, however, because different fabrics shrink quite differently. The higher shrinkages would be too great, and a finisher could not readily make adjustments from one kind of cloth to another.

Hence, it would obviously be best to use caustic of ordinary mercerizing strength, to process the cloth over a mercerizing tenter, and then to divert it to such special treatment as wet calendering. Practical conditions were best simulated in the laboratory by treating cloth on frames, as described, and washing well before its removal. When the fabric was so treated and calendered wet, a very bright glaze finish resulted which broke down upon deglazing to a high luster, much higher than obtained by mercerizing alone. This finish was not as smooth as desired, but withstood dyeing surprisingly well, or deglazing by an open boil, and retained a high luster. A tendency to remain stiff apparently could be easily overcome. Even though it withstood boiling so well, a finish of this type did not resist severe washing.

However, the process described might yield a finish of very high luster of more than moderate durability. A sateen yielded an especially striking lustrous finish of this type; any such product from a finishing plant would require especially careful evaluation for resistance to washing.

It seemed unlikely from experience that preswollen cloth could be calendered while containing dilute caustic solutions but, since it was suggested by a patent, a few experiments were made. It had been reported [2] that mercerized cloth washed with a 5–6% caustic solution was still swollen nearly twice as much as when the caustic was all washed out, or nearly four times as much as the unmercerized cotton merely swollen in water (inferred from centrifugal retentions). In a specific experiment, cotton mercerized with 20% caustic and washed with a 6% solution had 92% retention when squeezed-out on the calender. This illustrates again the very forceful and great amount of swelling that can be attained. It was found, however, from this and less extreme experiments that such preswollen cloth, even with

only a 2% washing solution, was too soft and became distorted and torn when pressed cold in the calender. It was obvious that such goods could not be wet calendered.

Further experiments on preswelling, usually with 20% caustic, and with softening or fixing agents added before calendering, are described below.

It has been generally true that the smoothness of finishes based on preswelling in caustic soda has not been as durable as when based on the other swelling agents, sulfuric acid or Cu-en.

Treatments with Sulfuric Acid

Preswelling with strong sulfuric acid has seemed throughout to yield the smoothest finishes, which also had other desired properties. In spite of obvious objections to its use in a plant, the acid has been tried alone at various concentrations and with the addition of 1–8% formaldehyde.

The action of formaldehyde-sulfuric acid mixtures on cotton is a field of research in itself. Very interesting dye effects were obtained, but no really useful result was found in connection with the swelling of cotton beyond what could be obtained with the acid alone.

Neutral salts have been suggested for addition to concentrated sulfuric acid to reduce its activity. The effect in an experiment was, as expected, to yield about the same result as obtained more simply by the use of a weaker acid.

Incidentally, cloth from one of the early typical treatments with the acid alone was tested for the formation of sulfuric acid ester of cellulose; none was found.

Experiments were made with sulfuric acid solutions through a range of 50–80% concentration, but finally centered around 63%. This is approximately the so-called mercerizing strength of sulfuric acid, and is within a range (62–64%) where there is a rapid increase in swelling [5]. The most acceptable conditions have been treatment for 45 sec. at 80° F. in the 63% acid. The concentration should be closely controlled by chemical analysis, but small departures from the other conditions have not been too critical.

The swelling that takes place in the 63% sulfuric acid is not like that in caustic of mercerizing strength (20–23%). In a specific comparison there were about equal retentions of water by samples of cotton cloth swollen in 20% sodium hydroxide and in 63% sulfuric acid after each had been washed and squeezed out in the calender. While the equal retentions seem to represent similar degrees of residual swelling, the cloth from the sodium hydroxide dyed much darker when the two were colored in the same bath, which implies that it was much more swollen. In contrast, as an indication of greater swelling by the sulfuric acid, cloth was so swollen during immersion in it as to be much weaker than cloth while in the alkali. The print cloth on pin frames in acid always tore in short slits in the warp direction, perpendicular to the line of pins. The swelling and shrinking forces were so great, and the cloth so weak, that the stress was relieved in this way. Such tearing has never been observed with the other swelling agents. Whether sulfuric acid of 63% concentration actually swells cotton more or less than the alkali, it has been found after washing to have shrunk the cloth less.

The ultimate result following preswelling in the sulfuric acid has been a return of strength to the cloth when it has been washed, calendered, and deglazed (Table II), apparently in accordance with statements that cotton will withstand 63% acid for several minutes without loss of strength. The temporary weakness might cause difficulty in practical processing under tension. On the other hand, cloth which actually tore at the pins was found to have finished with a gain of nearly 50% in tear strength over the untreated material.

Preswelling with 63% acid and wet calendering yielded fabrics with durable high luster, but offered no apparent advantage over the use of the more practical sodium hydroxide for such a finish.

Many of the experiments with sulfuric acid were

TABLE II. Properties of Finished Fabrics *

Number	Preswelling agent	How calendered	Coef. of friction, deglazed	Strength (tongue-tear), lb.
Plain cloth	—	—	1.26	2.13
1061	Sulfuric acid, 63%	Dry	.93	3.28
1062	Sulfuric acid, 63%	Wet	.62	—
1063	Caustic, 20%	Dry	1.08	—
1064	Caustic, 20%	Wet	.90	—
1065	Cu-en, .225 *M*	Dry	—	3.50
1066	Cu-en, .225 *M*	Wet	.71	4.69
Pilot run	Cu-en, .225 *M*	Dry	.5	1.39

* Each finished sample had 3% Zelan AP applied to the wet preswollen goods before calendering.

repeated on mercerized cloth but gave no promise of easier control or other advantages over unmercerized cloth. Improved smoothness was obtained as described below.

Treatments with Cupri-Ethylene Diamine

The use of cupri-ethylene diamine (Cu-en) was suggested by the familiar attempts to use cuprammonium solutions for cotton finishing. The Cu-en has the advantage of freedom from the strong ammonia odor. It should not be prohibitive in cost because the solution used contains only about 1½% copper and 3% ethylene diamine.

As noted earlier, when cloth was washed and squeezed after preswelling in 0.25 *M* Cu-en, its residual swelling was apparently considerably less than that due to the usual strengths of caustic soda and sulfuric acid (Table I). Consistently, it did not dye as dark a color when in the same bath with the caustic-treated material; inconsistently, it dyed about the same as cloth from sulfuric acid, which appears to have been much more swollen. In other words, its swelling is different from that of either of the other agents although results of its use have sometimes been substantially the same.

When the cloth, preswollen in 0.2–0.25 *M* Cu-en and washed, was wet calendered, it yielded a glaze finish which broke down to a durable luster upon boiling or dyeing. Again, while it seems fair to call these finishes durable, they will not withstand too much laundering. For attaining luster alone, there would be no apparent advantage in Cu-en over caustic soda, and there was no advantage in the use of mercerized as compared with unmercerized cloth as the base fabric.

Smoothness and Discussion of Results

Since many of the experiments in which additive finishing agents were padded onto the preswollen cloth were run with the three main swelling agents in parallel, they can be discussed together. These agents were usually 20% sodium hydroxide, 63% sulfuric acid, and 0.225 or 0.25 *M* Cu-en.

In representative experiments, print cloth was preswollen with one of these agents, padded to contain about 3% Zelan AP when squeezed to the usual pick-up, and calendered wet. The immediate results were very smooth finishes, but the fabrics were stiff and sometimes translucent. As judged from difficulty of wetting and resistance to deglazing, these finishes should be relatively stable. Since, at this stage, they were not of the type of smooth fabric desired, they have not yet had any particular consideration for possible uses.

When these finishes were broken by boiling for 30 min. as described earlier, extremely lustrous finishes resulted. All remained slightly stiff, and differences in appearance and hand were small. It is difficult to report on smoothness, since the only available measure does not correlate with the feeling of smoothness. Coefficients of friction recorded in Table II are quite high, but smoothness seemed much better than indicated by the figures. Smoothness by feel fell in the same order as by measurement; the sample preswollen in sulfuric acid was smoothest, and that from caustic soda least smooth by a small margin.

Although relatively durable to boiling water, the luster was lost rather rapidly upon repeated washing. There remained, however, a pronounced sheen, very distinctive from the original cloth and very durable. The sulfuric acid treated sample was particularly soft and smooth and seemed to have met the requirements of the smooth finish, although wet calendering with Zelan present is of doubtful practicability.

Other samples, preswollen and padded in Zelan as described above, were dried and calendered dry instead of wet. When deglazed at the boil they came out less lustrous but softer and smooth. The finish by this method has been at its best with sulfuric acid as preswelling agent. When the cloth was deglazed at the boil, especially by dyeing, it came out as one of the smoothest and softest of lustrous finishes. It retained a pronounced sheen after deglazing plus five washes, and was still smooth and soft. This was a smooth finish of the desired type without the disadvantages of wet calendering, including that of excessive stiffness. The latter was less noticeable in dry calendering, when fibers stick together less. Lack of exact reproducibility was probably due mainly to small variations in acid concentration, the importance of which was not fully realized. If this finish could be produced in a practical way, it would seem suitable for linings and some other apparel fabrics.

It is possible that Cu-en could be made to yield a similar smooth finish if the use of sulfuric acid should seem too objectionable. This was indicated

by one excellent result from a pilot plant run. The cloth was treated for 2 min. in a continuous machine in 0.225 *M* solution, padded through Zelan AP to about 3% content, dried, and calendered dry with normal tension on the goods. This run netted about 30 yd. of glazed material which was not excessively stiff and had a finish which was easily broken to a new, very lustrous smooth finish. While this was very promising, the result may have been influenced somewhat by degradation, which may contribute to durable smoothness. The loss of tear strength (Table II) was attributed to a shortage of sodium acetate in the Zelan bath rather than to anything inherent in the process. There was no difficulty with this run, and it would not seem impractical if continuous treatment in Cu-en can be suitably controlled.

The less promising preswelling by caustic soda offers the least departure from ordinary finishing processes for possible use with Zelan. The treated cloth might be calendered partially dry to advantage if a moisture level between dryness and wetness can be found at which Zelan will not come off on the calender rolls.

As might be expected from a report by Mazzeno and coworkers [8], fabrics which were finished with Zelan soiled more easily than plain cloth without Zelan. When tested by approximately their method, with soap as a detergent and carbon black present, absorption of carbon reduced the reflectance of the plain cloth only from 85% to 81%. The reflectance of Zelan-treated samples dropped from 81–84% to 54–64%; they were obviously badly soiled.

Sufficient tests have been made on strengths of finished fabrics of best smoothness to show that fabrics preswollen, padded with Zelan, calendered, and deglazed had higher tear strengths than the original cloth.

Much of the research is summarized in Table III, where observed values for smoothness (coefficient of friction) and stiffness are shown, these values representing individual experiments or averages from 2 to 5 experiments as indicated. Such observations aided particularly in judging effects from changes of different variables in the processes. They give some clues as to the characteristics of the finishes produced, but tell little about their real nature.

On the basis of this record, preswelling by Cu-en should lead to the most durable smooth finish. On the basis of feeling of smoothness, preswelling by sulfuric acid seemed to yield slightly more favorable results.

The production of dyed goods with such finishes as described would be a specific problem for any given set of plant conditions, with results not completely predictable from laboratory work. The routine dyeing test after calendering served as the scour usually needed after a Zelan finish, and it might seem that it could serve at this point in a practical process for all three purposes—scouring, breaking the finish, and coloring. Owing, however, to difficulty of wetting; to reduced accessibility to

TABLE III. Typical Observations on Experimental Finishes

Number	Kind of cloth	Preswelling agent	Zelan AP, %	How calendered	Coef. of friction calendered		Stiffness (drape flex), calendered	
						Dyed		Dyed
1017	Unmerc.	Water	—	Wet	0.24	0.77	1.14	0.64
992	Merc.	Water	—	Wet	.24	.87	1.05	.57
1028	Merc.	Water	3	Dry	.31	.85	—	—
948	Merc.	Water	2	Wet	.34	.91	.94	.59
Av., 5	Unmerc.	20% Caustic	—	Wet	.24	.74	1.18	.74
Av., 2	Unmerc.	63% Sulf. acid	—	Wet	.21	.67	1.32	.7
Av., 2	Unmerc.	.25 *M* Cu-en	—	Wet	.21	.44	1.19	.73
Av., 2	Unmerc.	20% Caustic	3	Wet	.3	.71	1.0	.67
Av., 3	Unmerc.	63% Sulf. acid	3	Wet	.28	.6	1.3	.77
937	Unmerc.	.25 *M* Cu-en	3	Wet	.28	.43	1.08	.73
1029	Unmerc.	20% Caustic	3	Dry	.29	.85	—	—
963	Unmerc.	63% Sulf. acid	3	Dry	.29	.65	1.09	.58
965	Unmerc.	.25 *M* Cu-en	3	Dry	.20	.43	1.14	.68

dye and possible unevenness from nonuniformity of finish; to tendency to dye only light shades; and to difficulty to be expected in controlling both shade and breaking of finish at the same time, dyeing after calendering obviously would not be practical.

As one alternative, goods dyed with some vat dyes under normal conditions would withstand one or another of the preswelling agents, and could be finished according to any of the procedures found to be otherwise acceptable. It is assumed that changes of shade due to processing could either be allowed for or tolerated.

A third, and in some ways preferable, procedure would be to dye the goods while still wet after the preswelling, and then finish as desired. The highly swollen cotton should dye very economically, owing to a relatively high affinity for the colors, but would tend to dye abnormally rapidly. The swelling would have to be very uniform, and trouble might follow if the goods became partially dried while preswollen, before dyeing.

Goods previously dyed have been finished in the laboratory, and dyeings made according to the methods suggested, before calendering. It seems quite possible that fast-dyed cottons can be finished as described.

Conclusions

In the investigations in the field of preswelling of cotton piece goods followed by calendering wet or dry, "finishes" have been discussed, although no samples were actually completely finished. Such steps as final softening, tentering, or an extra calendering would be needed under plant conditions. Hence the results reported must be recognized as laboratory finishes which may not be reproducible exactly as described and are presented to tell what was obtained, rather than just what can be done with it. It seems probable, however, that some of the best results could be improved in a finishing plant. For example, more favorable calendering conditions may be available, such as much higher pressures.

Some very smooth finishes have been obtained, so it has been shown that the production of the desired smooth cottons is possible. Optimum details under any particular laboratory conditions have not been worked out because this would have to be done again for any finishing plant. High luster and high strength are features not to be overlooked. Some of the finishes characterized by glaze were very smooth, and there were different degrees of stiffness, most of them outside the range of apparel fabrics. In general, the finishes have had limited durability to washing, although they withstood boiling to a surprising degree.

Since promising finishes were obtained with preswollen cloth calendered dry, as well as wet, it would seem logical to continue research in an intermediate field between dry and wet calendering. This might extend between regains of present practice and the lower of the regains in the wet calendering of preswollen fabrics. Advantages might be found from the preswelling, without the disadvantages of excessive amounts of water.

Attention has been called to methods which seem promising for further development to obtain high degrees of smoothness in cotton goods together with improved luster.

Acknowledgment

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Fiber Structure and Mechanical Properties of Untreated and Modified Cottons[1]

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Abstract

A brief review of investigations relating fiber structure to mechanical properties of cotton is given. The relationship of fibril alignment, as measured by the x-ray technique, to the strength and elongation properties of cottons covering a wide range in physical properties is discussed.

Alteration of mechanical properties of cotton brought about by degradation in hydrochloric acid, mercerization, decrystallization in ethylamine, resin treatment, and acetylation are related to changes in the fiber structure. The effects of stresses imposed during some treatments are discussed.

Introduction

Efforts to improve cotton textile products by breeding or by chemical treatments will become more productive if a thorough understanding of the relation of important fiber properties to the structure of the fiber is available. Research investigations at the Southern Regional Research Laboratory and elsewhere have been directed towards securing information on the effects of the gross and fine structure on the mechanical properties of the fibers.

A brief review of the fiber structure from the smallest element to that of the entire fiber is appropriate at the beginning of such a discussion. The average cotton cellulose chain molecule has a degree of polymerization of over 5000 and thus is over 3 μ in length. The chain molecules are organized into fibrils and lie more or less parallel to the fibril axis [17]. The smallest fibrils (microfibrils) generally observed in electron micrographs of cotton fibers which were beaten in water are a few hundredths of a micron across and contain about 500 chain molecules in cross section. Most fibrils are several times as large as the smallest detected in the micrographs. While cotton, like ramie, is relatively crystalline, there are disorganized chains and crystal surfaces which are accessible for moisture sorption, dyeing, and other processes.

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[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

The location of noncrystalline material in untreated and treated cotton undoubtedly has some influence on the mechanical properties. Figure 1 shows, in a much oversimplified manner, the possible locations of noncrystalline portions of polymeric fibers. The concept of amorphous regions within the fibrils of many fibers (Figure 1A) is supported by results obtained in investigations of the levelling-off degree of polymerization (LODP) [8], by electron micrographs of fibrils impregnated with heavy atoms [3], and by other techniques. However, the natural cellulosic fibers appear to be less distinct in this respect than many synthetic fibers. The existence of long or continuous crystals (Figure 1B) may not be expected where crystallization occurs from many minute nuclei, as is possible in some synthetic fiber processes, but may be the usual case for natural fibers. Figure 1C is probably more realistic, since it contains branched crystals as well as disorganized chains between and occasionally within fibrils. The structure is similar to the branched chain model described by Hearle [5].

The gross structure of the cotton fiber (Figure 2) is also important in its mechanical behavior. The fibrils in cotton are deposited in daily growth rings, as shown in Figure 2A. The dried fiber is a collapsed tube the shape of which varies greatly between and along each fiber (Figure 2B). The two outer layers, which are first to be formed, are quite thin and probably have little direct effect on the tensile properties of the fiber. The inner layers, which constitute a majority of the fibrils, are oriented in a

spiral direction around the fiber axis (Figure 2C), all layers spiralling in the same direction and all reversing together at irregular intervals. Sisson has shown that a relative measure of the spiral angle could be made from azimuthal tracings of x-ray diffraction, the so-called x-ray angle [15].

The fiber structure is further complicated by variations in cross-sectional shape and area along the fiber length. These variations, along with reversals, kinks, abrasions, and other imperfections, make the cotton fiber very nonuniform in strength and elongation along its length. Thus, cotton fiber strength depends greatly on the length of the section being tested. The drop in mean single fiber strength with gauge length follows from the statistical considerations explained by Peirce [13]. Different cottons have different relationships of strength to gauge length. They may even reverse their positions with change of the test length used.

The bundle tenacity is always lower than mean single fiber tenacity but can be calculated from single fiber stress–strain data [9]. The percent change in either single fiber or bundle tenacity between two gauge lengths is considered as a measure of the uniformity of strength along fiber length. Small changes indicate uniform fibers. The percent decrease in tenacity with increase in gauge length is essentially equal for single fibers and bundles [11].

Untreated Cottons

The relation between bundle strength and the x-ray angle measurement of fibril alignment has been given by Sisson and others [1, 15]. In further investigations at this laboratory, 32 cotton samples were selected to cover a wide range in mechanical properties and fine structure. The selection, insofar as possible, made each property independent of the others. In Figure 3, the relationship of bundle tenacity at the gauge length given by $\frac{1}{8}$-in. spacer to x-ray angle is shown for two of the three groups of cottons classified according to uniformity of strength along fiber length. A similar dependence of the relationship on uniformity of strength along fiber length was shown by Rebenfeld and Virgin [14]. In Figure 4, the relationship is less dependent on uniformity, and the overall correlation is improved. An estimate of the effective gauge length with zero spacer is about 0.5 mm. [9].

If the tenacity–gauge length relationship of each cotton is extrapolated to a gauge length of about 0.1 mm., a measure which approaches the "intrinsic strength" of the fiber is obtained (Figure 5). This intrinsic strength is quite high and appears to be dependent only on the x-ray angle, regardless of the other properties of the cotton or of the variety or growth conditions. The correlation coefficient for the 32 cottons was 0.90.

The x-ray angle has also been shown to influence the modulus and elongation of cotton [4, 7, 15]. In Figure 6 is shown the relationships between the bundle secant modulus ($\frac{1}{8}$-in. spacer) and x-ray angle. As was shown for tenacity, the relationship was found to be dependent on the uniformity of strength along the fiber length. If bundle elongation could be measured accurately at shorter gauge

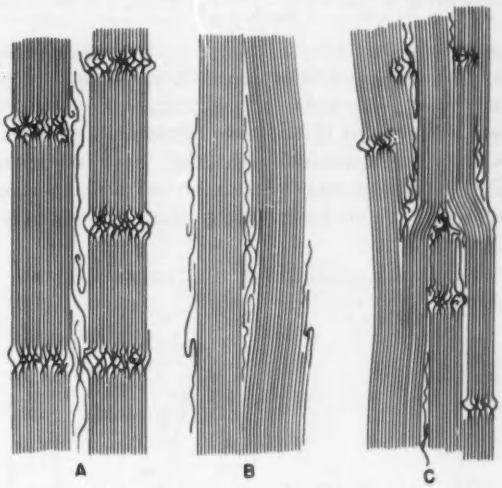

Fig. 1. Schematic representation of several possible crystallite structures.

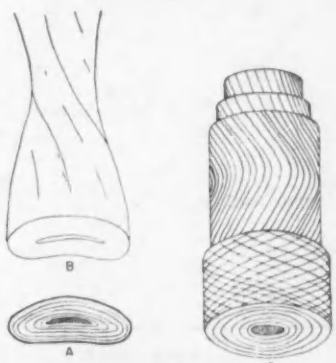

Fig. 2. Sketches showing gross structure of cotton fiber. (A) Cross section; (B) longitudinal; (C) internal.

lengths, presumably a similarly high dependence of modulus on x-ray angle would be found.

The elongation at break, which depends upon tenacity and secant modulus, is correlated also with x-ray angle, as shown in Figure 7. Since cotton, like ramie, is relatively crystalline, it has long been apparent that much of the elongation of cotton results from the spiral structure. Unlike the spiral structure of a yarn, however, the reversals in the fiber allow it to untwist when load is applied. This can be observed during the untwisting of a short length of fiber having predominantly either left or right hand spiral when a free hanging load is applied. The theoretical elongation expected from the untwisting of fibers $\left(\frac{1}{\cos\theta} - 1\right)$, where θ is the x-ray angle, is shown also in Figure 7. The discrepancy between theoretical and measured elongation can be attributed to the facts that the x-ray angle is only a relative measure of the true spiral angle and that twist in the structure is not entirely removed before fiber rupture occurs. Thus, the calculated elongation was found to be higher than the observed elongation.

It is apparent from the strength relations that the efficiency of cooperation of the fibrils in a cross section is reduced by the spiral structure. Thus, at a very short gauge length, strength decreases and elongation increases with increase in spiral angle. However, since the effective grip lengths in practical structures as yarns or fabrics are probably greater than that at zero spacer or below, attention should be given to causes for nonuniformity of strength along fiber length. Any nonuniformity or weak spot which reduces both strength and elongation of the fiber is of great practical significance.

One source of weak points is the reversals in spiral structure [18]. The number of reversals per centimeter was found to correlate with the tenacity for low x-ray angle cottons (Figure 8). The large angle cottons were all of low strength. There are other causes of weak places along the fiber length, but no practical way has been found to measure and express them mathematically. In general, fiber strength is directly correlated with staple length and inversely with fiber linear density. This makes length and linear density doubly important, since both contribute to yarn strength independently of their relations to fiber strength.

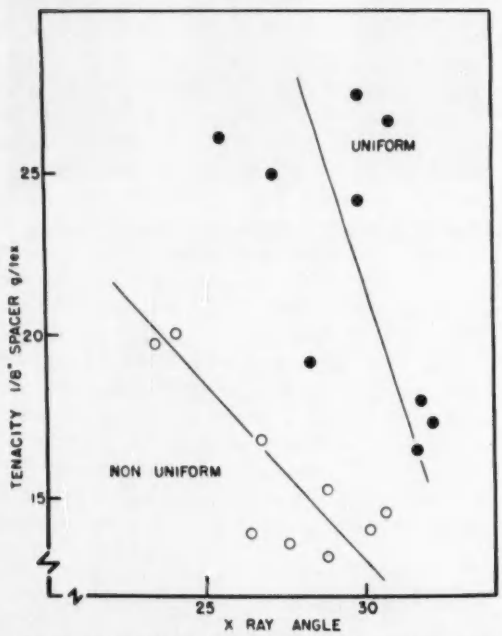

Fig. 3. The relationship between bundle tenacity at $\frac{1}{8}$-in. spacer and x-ray angle for the selected uniform and nonuniform groups of cottons.

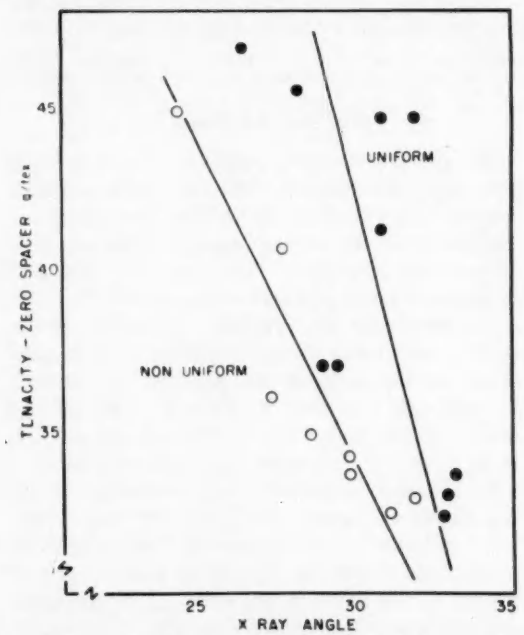

Fig. 4. Relationship between bundle tenacity at zero spacer and x-ray angle for the selected uniform and nonuniform groups of cottons.

Elastic recovery investigations of untreated cotton fibers and yarns show that about 50% of their extension is permanent set when they are strained to 5% of their length. Untreated cotton fibers appear to behave as relatively crystalline coiled springs with some friction between the springs. Wetting the fibers or yarns results in recovery of most of this "permanent set" elongation, possibly by lubrication between fiber elements where water can penetrate.

Cellulose Degradation

The conception of behavior of structural elements and causes for weak places in the fibers must be altered to some extent when we consider some chemically or physically modified cottons. Considerable interest exists in the mechanism of mechanical breakdown when cotton is degraded by heat, moisture, acid, or other agents that sever the cellulose chain molecule. The oversimplified model for celluolse structure of Figure 1A can be used to illustrate and to discuss this mechanism, since it is easiest to treat theoretically. It is not considered either accurate or rigorous. A branching crystal model similar to Hearle's [5] is probably more nearly correct for untreated natural fibers. In any case, fiber strength is visualized as being proportional to the combined strength of the individual cellulose chain molecules aligned parallel in fibrils. Load is transmitted from chain to chain along the fiber by mutual bonding between the chains in the crystalline regions and to some extent in the noncrystalline regions. In the case of hydrolysis, only the noncrystalline regions and crystal surfaces are accessible for chain breakage. The loss of strength is visualized as resulting mainly from rupture of chains connecting relatively protected crystalline regions in a fibril. The rate of breakage of unbroken connecting chains in an amorphous region is given by $dN/dt = NRD$, where N is the number of unbroken connecting chains and D is the length of an amorphous region connecting crystallites. R is a rate constant depending only on the degrading conditions of temperature, etc. and is considered a constant in this analysis when less than 1% of the available links are broken. The length D may be expressed as the crystallite repeating length L multiplied by the amorphous fraction A. Therefore,

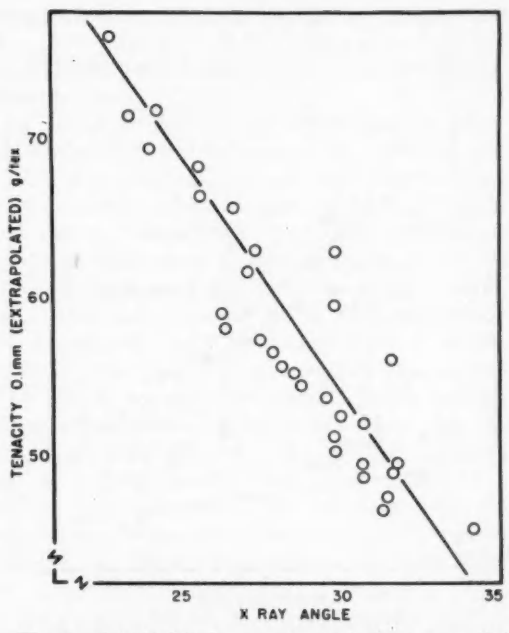

Fig. 5. Relationship between the intrinsic strength (0.1-mm. gauge length) and x-ray angle for cottons, irrespective of uniformity.

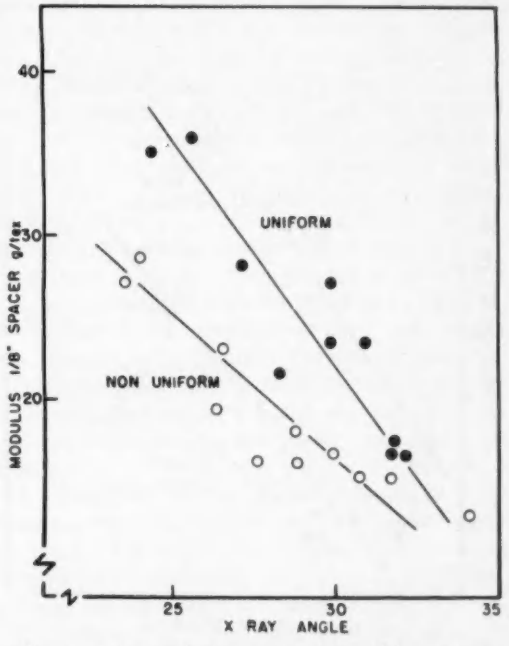

Fig. 6. Relationship between secant modulus and x-ray angle for selected uniform and nonuniform groups of cottons.

$-dN/dt = NRAL$. Integrating between proper limits gives $N = N_o e^{-RALt}$, where N_o is the original number of chains connecting crystallites and t is the time. Since RAt is the fraction of total bonds broken, B, which can be estimated from the decrease in degree of polymerization, $B = 1/P_t - 1/P_o$, where P_o and P_t are the DP of the original cellulose and the degraded cellulose respectively. Then $N = N_o e^{-BL}$. Assuming that strength S is proportional to the number of chains remaining unbroken, $S = S_o e^{-BL}$.

This is essentially the equation derived by Sippel [16] and expresses mathematically the concept of Conrad et al. [2]. From strength and viscosity data, the calculated length L should be of the same order as the levelling off degree of polymerization.

Such comparisons for cotton, mercerized cotton, ramie, and viscose rayon were reported by Tripp et al. [17]. The considearble discrepancy between the calculated crystallite lengths and LODP measurements is to be expected because of oversimplification in the analysis and possibly errors of measurement. However, the analysis explains the relatively large drop in strength of untreated cotton as compared to mercerized cotton or rayon at comparable percentages of total links broken.

The other effects of degradation are reduced elongation and decreased uniformity of strength along fiber length. The latter is given in Table I for untreated and mercerized fibers. Degradation in 5 N HCl at room temperature consistently reduces strength uniformity, causing the percent strength loss to be different at different gauge lengths.

Chemical Modification

In studies of methods of altering fiber structure for more favorable mechanical properties, consideration should be given to mercerization and decrystallization with ethylamine. Each process involves swelling of both amorphous and crystalline regions of cotton and results in considerable decreases in crystallinity. Mercerization increases the uniformity of strength along fiber length [11]. The intrinsic strength (at short gauge lengths) is not greatly changed in cotton mercerized while held at its original length. The apparent decrease in tenacity for slack mercerized cotton can be accounted for by the very high elongation. If the linear density were measured at the moment of rupture, differences in the tenacity of mercerized slack and mercerized with

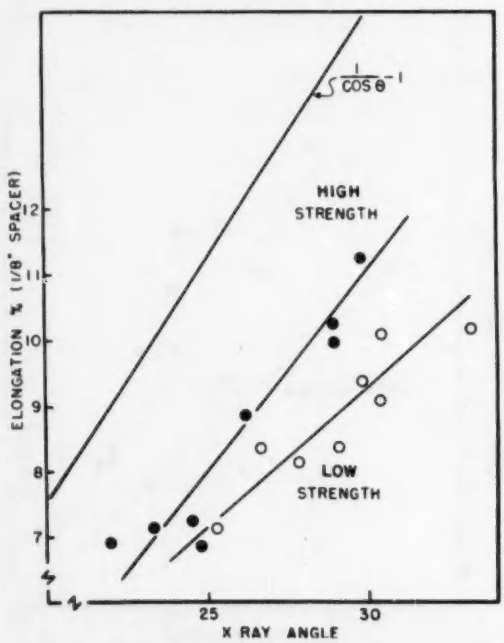

Fig. 7. Relationship between bundle elongation (⅛-in. spacer) and x-ray angle for the highest and lowest strength groups of cottons.

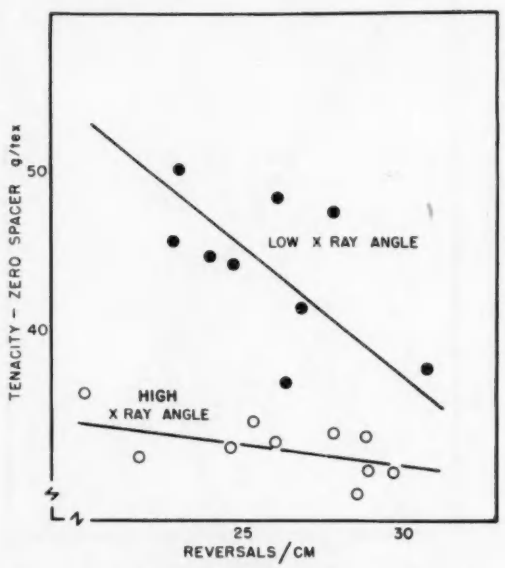

Fig. 8. Relationship between bundle tenacity with zero spacer and reversals per centimeter for the lowest and highest x-ray angle groups from 32 cottons.

TABLE I. Strength Losses of Cotton Fibers on Degradation in 5 *N* Hydrochloric Acid

Treatment	Tenacity			Strength retained	
	Zero spacer, g./tex	¼-in. spacer, g./tex	Decrease, %	Zero spacer, %	¼-in. spacer, %
Scoured					
Untreated	32.9	19.2	42	100	100
Degraded 4 hr.	21.4	10.8	49	65	56
Degraded 8 hr.	16.6	8.2	51	49	43
Mercerized (slack)					
Untreated	27.0	19.8	27	100	100
Degraded 4 hr.	20.0	12.3	38	75	62
Degraded 8 hr.	16.8	8.7	48	62	46

tension would be small. The change in tenacity then appears to be largely a matter of repair of weak places along the fiber length similar to an annealing process, and takes place both with and without tension.

Slack mercerization greatly increases the elongation of the cotton fiber. Although ethylamine lowers the crystallinity possibly more than mercerization, there is much less contraction in fiber length in the slack treatment with ethylamine than with sodium hydroxide, and consequently much less increase in elongation. In addition to changes in tenacity and elongation, large changes in modulus and toughness illustrate the great change of properties achieved by these treatments [11, 12].

A possible explanation for differences in swelling and contracting behavior of cotton in ethylamine and sodium hydroxide was obtained, with some difficulty, through investigations of short lengths of fiber in both swelling media [11]. The total volume swelling in ethylamine is essentially the same as the change in volume of the crystalline fraction as deduced from x-ray studies, but in 19% sodium hydroxide solution the total volume swelling is considerably more than that in the crystalline fraction. This may be interpreted to mean a larger swelling in the noncrystalline portion in NaOH, causing the chains or other fiber elements to take a zig-zag course in fibers swollen slack and resulting in a higher contraction than can easily be explained otherwise. Permanent set at strains near break is large in slack treated samples, especially those which are mercerized. Tension during treatment, which reduces permanent set, also reduces total elongation [12]. The x-ray angle of slack treated samples is essentially unchanged from that of the untreated, but tension during treatment causes a significant decrease in the x-ray angle.

Physical properties are greatly changed by resin treatment [17], and tension during curing of the resin affects both the tensile and elastic properties. Slack treatment results in a large decrease of fiber and yarn strength, while resin treatment with high tension during the cure may increase yarn strength. Unfortunately, for many textile uses, a serious loss of elongation is found in the high tension treatment, resulting in brittle fibers and yarns. Fibers from yarns resin treated with tension have bundle strengths near those of the untreated. The strength loss found in the slack treatment is not the result of chain breakage, since strength can be essentially restored by partially removing the resin. Therefore, the great loss in strength in the slack treatment must result from chemically or physically cross-linking the fiber elements (chain molecules, fibrils) in unfavorable positions for equal stress distribution.

The large reduction of x-ray angle in fibers from yarns resin treated with tension is shown in Table II. Fibers from slack treated yarns have x-ray angles near those of the untreated. These x-ray measurements were made after a mild detergent washing which partially restored a similar reduction in x-ray angle of fibers from yarns mercerized with high tension.

A comparison of the tensile behavior of resin treated cotton with that of acetylated cotton is appropriate. The breaking loads of fibers or yarns are changed only moderately at standard conditions, whether the acetylation treatment is slack [10] or with tension [6]. The slack treatment increases elongation and permanent set. The fiber elements are apparently not tied together by acetylation but

TABLE II. The Effects of Tension During the Treatment of Cotton Yarns with Aerotex M-3 on the X-Ray Angle and Tenacity of the Fibers

	Tension			
	Slack		High*	
Sample	X-ray angle, ½ maximum, degrees	Tenacity, ½ in. gauge, g./tex	X-ray angle, ½ maximum, degrees	Tenacity, ½ in. gauge, g./tex
Pima S-1	31.7	13.7	22.8	24.4
Bobshaw	32.5	8.3	22.4	17.2
S × P	30.9	13.0	22.1	23.5
Hopi Acala	26.6	16.4	21.3	20.0

* Slightly below breaking load.

are apparently freer to move than they are in very dry cotton where hydrogen bonding seriously interferes with stress equalization in the fiber.

These investigations of fiber structure and mechanical behavior point out some of the significant differences in fiber structure of untreated cotton, the further differences that can be achieved by various chemical treatments, and the importance of certain physical factors such as tension during these treatments. The effects of these variations in fiber structure on some tensile properties have been discussed. The general approach of attemptinng to understand the way chemical treatments bring about the various changes in physical properties should lead to better directed efforts to improve cotton textile products.

Acknowledgments

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Permanent Set in Cotton and the Physical Mechanism of Wrinkle Resistant Treatments[1]

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WHEN a cotton fiber is stretched and the stretching force removed, it does not come back to its original length, even after indefinitely long periods of time. The residual, or unrecovered, elongation is one form of permanent set that can be imparted to textile fibers. The magnitude of the permanent set depends not only on the magnitude and duration of the load, but also on the amount of moisture in the fiber. A rough value for permanent set in cotton and rayon is in the neighborhood of 50%, in flax 35%, in Fortisan 30%, and in nylon 10%.

Considered from the standpoint of its physical properties, the cotton fiber is composed of three distinct, major types of structural elements. The accompanying photographs, which were taken by Miss Mary Rollins and her coworkers at the Southern Regional Research Laboratory in some of their studies of the structure of the cotton fiber, will be helpful in illustrating the manner in which these structural elements function.

Figure 1 is an idealized structure of the cotton fiber. What is known as the secondary wall, or secondary lamellae, with which this discussion will be concerned, comprises the bulk of the fiber, and its physical properties almost wholly determine the major physical properties of the fiber.

Figures 2 and 3 show two of the three major structural elements. The larger of these two elements, known as a growth layer, can be seen in Figure 2, which is a fiber cross section, highly swollen in the cellulose solvent cuprammonium hydroxide. The concentric lamella structure is clearly visible here.

The smaller of these two elements, known as a fibril, can be seen in Figure 3, which shows the surface of a fragment of one of the growth layers. Fibrils consist of bundles of a smaller element known as a microfibril. Their existence, though highly important, will not be dealt with at any length in this brief discussion, and the two terms will be used, loosely, somewhat synonymously. The smaller strands in Figure 4 are microfibrils.

The fibrils in each growth layer are closely parallel and, as is well known, they are spirally disposed around the fiber axis, with frequent reversals in the direction of the spiral. If there were no reversals in the direction of the spiral, the physical properties of the cotton fiber would be markedly different. In this structural feature of reversals lies one of the major differences in the physical properties of cotton and man-made fibers, and also in cotton and some of the other plant fibers.

The third and smallest of the three major structural elements of cotton, unless one wants to go all the way down to the unit cellulose cell or the glucose unit, is the cellulose molecule, or the cellulose chain. In cotton, these chains are bound together in a high degree of lateral order, and bundles of these highly ordered chains make up the microfibrils and fibrils.

Bearing in mind that the actual cotton fiber is not a straight, round cylinder, but a twisted, crimped,

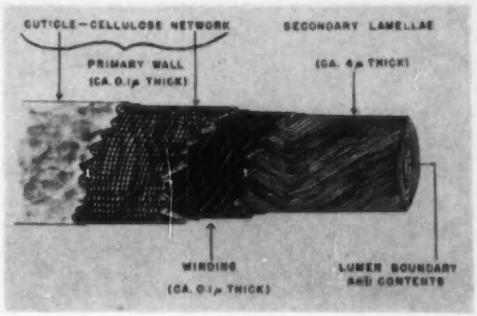

Fig. 1. Drawing of an idealized structure of the cotton fiber.

[1] Presented at the Cotton Chemical Finishing Conference, National Cotton Council of America, Washington, D. C., October 1–2, 1958.

[2] Present address: Agricultural Research Service, U. S. Department of Agriculture, Washington, D. C.

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partially collapsed tube, consider what happens when the fiber is stretched. Since the cellulose chain is relatively inextensible, some of the fiber's microscopic and submicroscopic structural elements must move relative to one another in order for the stretching to take place without the fiber breaking. When this relative movement is great enough, some of the structural elements slip into new positions of mechanical equilibrium and will not return to their former relative positions when the stretching force is removed. The result is permanent set.

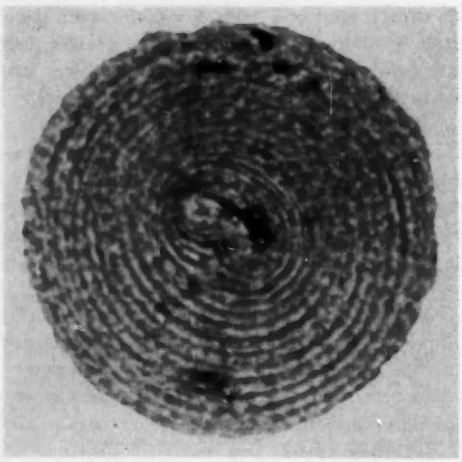

Fig. 2. Light microscope photograph of fiber cross section highly swollen in the cellulose solvent cuprammonium hydroxide, showing growth layers.

It follows that if certain of these structural elements are cross-linked or "tied" together with suitable agents, slippage among these elements under any given load will be reduced, thereby reducing the amount of permanent set; elastic recovery will be increased, thereby giving a more wrinkle resistant fabric. This assumes, of course, that the elastic properties of the fibers are transmitted to the fabric, and I believe there is today rather general agreement on this.

The foregoing is, obviously, an incomplete and oversimplified explanation of the mechanism of permanent set in the cotton fiber and of the mechanism by which cross-linking agents impart wrinkle resistance. However, it should be sufficient to illustrate the principles involved and serve as a basis for hypothesizing regarding which specific sets of structural elements in cotton must be cross-linked if wrinkle resistance is to be obtained.

Scientists working in this field seem to be in fairly good agreement with the statements I have just made regarding the *general* nature of permanent set and of the mechanism by which cross-linking agents make cotton more elastic, but when we get *specific*, the agreement ends.

We have, then, three different possible mechanisms, and combinations of these mechanisms, by

Fig. 3. Electron microscope photograph showing fibrils in a layer of the secondary wall.

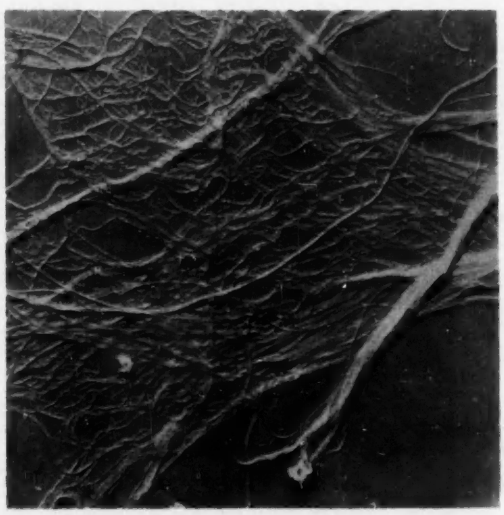

Fig. 4. Electron microscope photograph showing fibrils and microfibrils.

which the cotton fiber can acquire permanent set, and three different mechanisms, and combinations of these mechanisms, by which elastic recovery may be increased. We have possible slippage (1) between the structural elements of the fibrils and microfibrils (that is, between cellulose chains, groups of chains, and crystalline regions), (2) between fibrils, and (3) between growth layers. All three of these mechanisms can be operative simultaneously or in some sequence pattern, in which case their relative influence in determining the elastic properties of the entire fiber becomes a matter of both practical and scientific importance.

There is a wide diversity of opinion and belief regarding what structural elements are involved in permanent set and in cross-linking to obtain wrinkle resistance.

Following are a few brief observations regarding current thinking as to which structural elements are involved in permanent set and in cross-linking to achieve wrinkle resistance. I would like to propose that realtive movement between growth layers may contribute significantly to permanent set and that cross-linking between growth layers may contribute appreciably to wrinkle resistance.

There are frequent reversals in the direction of spiralling of the fibrils around the fiber axis. In addition to this unique structural feature, it has been rather well established that, beginning with about the second layer of the secondary wall, the reversals in the direction of the spirals in all subsequent layers occur at the same cross-sectional points along the length of the fiber. In commercial cottons there are about 25 to 50, or more, of these reversals per inch.

These two structural features cause cotton to have an essentially different mechanism of stretching from that of the man-made fibers, such as rayon and other high polymers, and different from that of some of the other plant fibers, such as flax. With such a structure, the stretching of the cotton fiber is accompanied by a tendency to simultaneous rotation, in alternating opposite directions, of adjacent segments associated with the reversals. In other words, each segment between two points of reversal actually untwists, with the segment on one side of a reversal untwisting in a direction opposite to that of the segment on the other side. As a consequence, a set of torques of alternating opposite angular direction is set up along the length of the fiber. When the load is removed, this set of torques tends to "retwist" the fiber and, together with the forces set up by a generally longitudinal stretching of the growth layers themselves, tend to bring the fiber back to its original length.

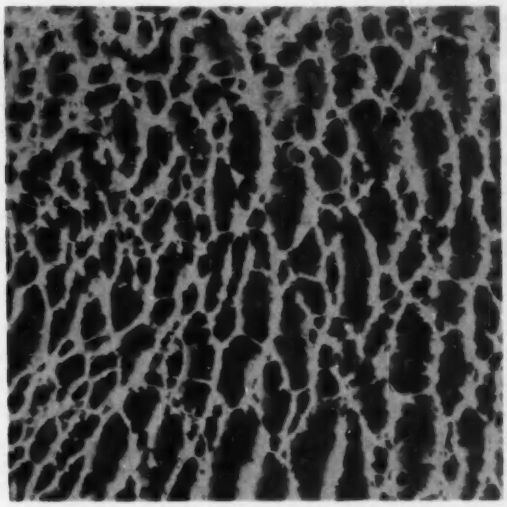

Fig. 5. Electron microscope photograph of cross section of fiber swollen with methacrylate, which is not a solvent for cellulose.

Fig. 6. Electron microscope photograph of fragment of secondary wall of cotton treated with a cross-linking agent.

Some people believe that permanent set in the cotton fiber is due to slippage between cellulose chains and crystallites within the fibrils. This is possible,

but when one considers that almost all of the observed extensibility of the cotton fiber can be accounted for by simple geometry as the untwisting and straightening out of the fibrils in the direction of the fiber axis, substantiation of this belief would require a very complex explanation. Similarly, the extent to which cross-linking these submicroscopic elements would be effective in reducing permanent set would depend in large measure on the extensibility and flexibility of the fibrils.

Others believe that most of the permanent set comes from slippage between fibrils and that cross-linking between fibrils is the major mechanism in reducing permanent set. This is certainly plausible, but there is still the question of the magnitude of this slippage. In this connection, reference to Figure 3 is pertinent. The surface of the secondary wall seen in Figure 3 is that of a fragment of a single growth layer obtained by mechanically breaking up the fiber in water in a Waring Blendor. The individual growth layers of the fiber are easily separated by this mechanical beating, but there is evidently a much stronger lateral cohesion between fibrils within growth layers which leaves sheets of the secondary wall like the one shown in Figure 3. The question is, how much slippage actually occurs between fibrils in normal stretching during usage, and by how much does additional cohesion provided by cross-linking reduce this slippage?

Last, we have the possibility of relative movement between growth layers as a significant source of permanent set and of cross-linking between growth layers as a means of significantly reducing it. I believe there is at least some relative movement between growth layers, and also an opportunity for a certain amount of slippage between them.

Figure 5 shows a cross section of a fiber swollen about 500% by polymerization of methacrylate in the fiber after preswelling the fiber in glycerine or water. There is little evidence of swelling of the fibrils themselves that compose the growth layers, which has important implications, but the swelling between the layers was so great that they have been physically separated by very large relative distances. It seems to be fairly well established that even at normal regains some of the absorbed water in cotton lies between the growth layers, as well as in other locations within the fiber. Since water is both a swelling agent and a lubricant for cellulose, it seems logical to assume that if there is a tendency toward relative movement between layers, then some slippage will occur when the fiber is stretched. Also, if these layers are cross-linked, the torques, or restoring forces, generated along the fiber by any given extension would be increased. This would be true, of course, if only the fibrils and microfibrils were cross-linked, or if the fibrils were made stiffer by cross-linking only between individual cellulose chains within the fibrils and microfibrils. The question remains as to how much of the permanent set in cotton fibers is due to slippage between growth layers, and to what extent cross-linking between layers reduces permanent set.

With our present knowledge, we do not have answers to these questions, but laying out the problem in this manner should be helpful in giving us clues to approaches that will lead, step by step, to a final solution.

Figure 6 illustrates one of the present difficulties and also one of the tools that might be of use in verifying our different theories about the physical mechanism of wrinkle resistant treatment; it shows a fragment of the secondary wall of a fiber treated with a typical cross-linking agent, obtained by beating the fiber in water in a Waring Blendor. This fiber came from a fabric that has good wrinkle resistance. The fragment is many growth layers thick, showing that the layers are cross-linked or bound together in some manner. There is visible evidence that the fibrils also are cross-linked. Lastly, there is no reason to believe that whatever "amorphous" cellulose there may be within the fibrils is not also cross-linked.

Since there is cross-linking between all of the major structural elements of the fiber, or at least some kind of bonding together, how can we say from this experiment which, if any, of the three possible mechanisms we have briefly discussed plays the dominant role in reducing permanent set? We can not, but by using this technique, and others, we should be able, in due time, to obtain an accurate knowledge of the true mechanism of permanent set in the cotton fiber and of the mechanism of wrinkle resistant treatments. As an example, we might develop, or discover, a cross-linking agent that does not tie the growth layers together but does give a strong bond between fibrils, as determined by beating the fiber in a Waring Blendor. Or we might develop or discover a cross-linking agent that bonds together only the chains within the fibrils and micro-

fibrils. The resulting physical properties of these treated fibers would provide useful evidence for assessing the relative importance of bonding together, or not bonding together, various combinations of these three major structural elements.

We who are working on the utilization of cotton hope that more concerted attention will be given by more people and organizations to solving this commercially important, basic problem. The sooner it is solved, the sooner can scientists proceed more intelligently in applying their specialized knowledge to developing more useful products from cotton.

Imparting Crease Resistance and Crease Retention to Cotton With APO[1]

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Abstract

Cotton fabric (80 × 80) was made crease resistant by processing with APO, tris(1-aziridinyl)phosphine oxide. Application was made by wetting the fabric with an aqueous solution of APO containing catalytic quantities of zinc fluoborate, squeezing out the excess with squeeze rolls, drying for 4 min. at 80–90° C., and curing for 4 min. at 140° C., followed by a good wash. An aftertreatment with a 1% Primenit VS[3] solution increased the crease recovery angle. Monsanto crease angles of from 250° to more than 300° (warp + fill) have been obtained, depending on the resin add-on. The crease recovery is not changed much by home laundering. A loss of 30% in the Elmendorf tearing strength was observed with samples with over 300° crease recovery angles. Creases durable to washing were obtained by drying the fabric with a hand iron followed by an oven cure. The resin could not be stripped from the fabric by methods that are effective with other resins. In addition to imparting crease resistance, this resin also imparts some degree of flame resistance.

COTTON garments are superior in comfort to those made from synthetic fibers, due to greater moisture regain and absorptivity, so it would be beneficial to add features such as wrinkle resistance without impairing the desirable properties. To obtain wrinkle resistant cotton, numerous so-called wash and wear resins are being used which fall short of meeting the almost unattainable ideal requirements for such a resin. Some of the disadvantages are low tearing strengths, poor durability, wet soiling, chlorine retention, and seam pucker [8].

The purpose of this paper is to present data on a new durable resin-forming monomer which appears attractive and which seems to overcome some of the objectionable features of the currently existing wrinkle resistant resins. This new textile finishing agent was based on a very reactive phosphorus compound, tris(1-aziridinyl)phosphine oxide, referred to as APO, which is one of the ingredients which when mixed with tetrakis(hydroxymethyl)phosphonium chloride, referred to as THPC, produces a very durable flame retardant finish for cotton [6]. It was through flame retardancy work that we first noticed the crease resistant properties which it imparts to cotton. APO was made by the reaction of phosphorus oxychloride with ethyleneimine, using an acid

[1] Presented at the Cotton Chemical Finishing Conference, National Cotton Council of America, Washington, D. C., October 2, 1958.

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[3] This name is given for convenience only and is not to be construed to be a recommendation by the U. S. Department of Agriculture.

acceptor like triethylamine in some inert solvent such as benzene [3]. Yields above 90% have always been obtained. APO, which has the structure as shown in Figure 1, is a white crystalline compound having a melting point of 41° C.; it is soluble in water and in a number of organic solvents. It is a monomeric trifunctional chemical, having three reactive positions (the three aziridinyl groups shown in Figure 1); it is capable of both resin formation and reaction with cellulose.

Since APO has three reactive groups, there are several ways in which it can react when applied to cotton. It can condense with itself to form a polymer, as shown in Figure 2 below, and can also react with the cotton cellulose to form an ether linkage as shown in Figure 3.

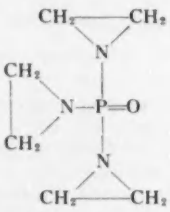

Fig. 1. Structural formula for tris(1-aziridinyl) phosphine oxide (APO).

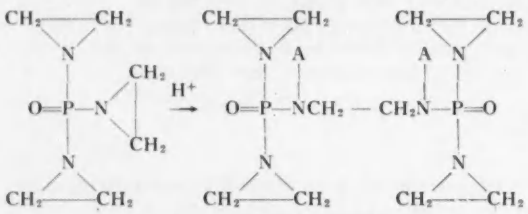

Fig. 2. Initial polymerization of APO;
A is H, or $-CH_2CH_2N-$.

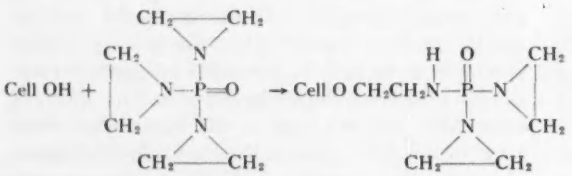

Fig. 3. Initial reaction of APO with cellulose.

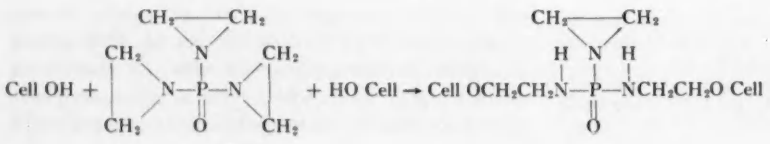

Fig. 4. Cross-linking of cellulose with APO.

After the initial reaction has taken place, there still exist two aziridinyl groups which are available and capable of reacting with a second hydroxyl group to cross-link the cellulose through ether linkages, as shown in Figure 4. The aziridinyl groups can also react with the hydrogen atom attached to the nitrogen as a result of the ring opening to form a highly cross-linked polymer, as shown in Figure 5.

The processing is very simple and can be done on standard resin finishing equipment. It consists of impregnating fabric with an aqueous solution of the resin-forming monomer by immersion and removing the excess solution by passing the wetted fabric through squeeze rolls. Heat (with the help of a catalyst) cures the water-soluble resin-forming monomer, producing an insoluble, highly cross-linked polymer inside the cotton fiber. The resulting fabric is crease resistant.

Materials and Methods

Most of the APO used in these experiments was prepared in this laboratory from phosphorus oxychloride and ethyleneimine, but some was obtained commercially as an 85% solution sold under the trade name Imine IP.[4] In order to work with the pure compound, it was necessary to isolate the crystalline product by stripping the solvent, using vacuum distillation. Some experiments were made, however, in which the Imine IP was used as received.

Most of the experimental work was done with a desized, scoured, and bleached 80 × 80 cotton print cloth, 3.2 oz./sq. yd. Other fabrics used included a desized, scoured, bleached, mercerized, and Sanforized broadcloth 140 × 64; a desized, scoured, and

[4] Use of a company and/or product named by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

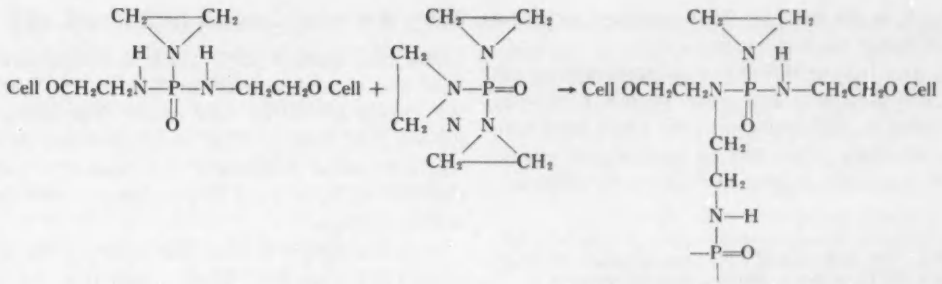

Fig. 5. Initial formation of polymeric APO attached to APO cross-linked cellulose.

bleached 8-oz. cotton twill fabric; a 5-oz. cotton poplin fabric, and a 2-oz. cotton lawn fabric.

An electrically heated forced air type oven was used to dry and cure fabric for most of the treatments. For full-width runs a forced-air, steam-heated oven was used.

Two types of softener and lubricating agent, Primenit VS (octadecyl ethylene urea) in a 20% emulsion and Quadrasoft E (a polyethylene resin emulsion containing 25+% solids), were evaluated.

The following six possible catalysts were screened:

1. Zinc fluoborate in 40% solution.
2. Boron trifluoride dimethylformamide complex.
3. Boron trifluoride ethylamine complex.
4. Tetrakis(hydroxymethyl)phosphonium chloride.
5. Triethanolamine.
6. Catalyst AC (an alkanolaminehydrochloride).

Catalyst concentrations used were based on the weights of APO in the treating solution.

Approximate resin add-ons were calculated from the air-equilibrated weight of the fabric

The resin stripping processes consisted of the urea-phosphoric acid method and the mineral acid hydrolysis method [7].

All physical testing was performed by ASTM methods, under the standard conditions of 70° F. and 65% relative humidity [2]. Wrinkle recovery angles were made with the Monsanto Wrinkle Recovery Tester [2] using a 500-g. weight. Phosphorus was determined by the colorimetric reduced molybdate method after digestion with sulfuric acid and hydrogen peroxide [5]. Nitrogen was determined by the Kjeldahl method using a mercury catalyst.

The samples were laundered in a typical agitator-type home automatic machine. They were washed at 50° C. (122° F.) in water containing a synthetic detergent, using a 40-min. cycle, which included the rinse and damp-dry cycles. All of the samples were tumble-dried in an electrically heated home dryer for 20 min. with the dial set at medium.

The soap–soduim carbonate treatment consisted of boiling the samples of fabric for 3 hr. in a solution composed of 0.5% standard soap [4] and 0.2% sodium carbonate, followed by rinsing and drying.

Experimental and Discussion

Influence of APO Concentration Upon Resin Add-On, Tearing Strength, and Crease Resistance

In order to establish the preferred amounts of APO to obtain wrinkle resistance, aqueous solutions of APO containing 1% Triton X-100 were prepared. The APO solids contents were varied from 8% to 28%, each solution increasing in solids by 4% increments. No catalyst was used in this experiment. Samples of 80 × 80 print cloth were padded through the various solutions using a tight nip so that the wet pick-up was approximately 80%. The samples were dried for 4 min. at 80–90° C. and cured for 4 min. at 140° C., then washed for 30 min. in hot tap water containing a detergent and rinsed, followed by drying. The increase in the weight of the resin treated fabric after equilibration is termed resin add-on. It is shown in Table I that when APO is used alone the efficiency, based on resin add-on, is very low. There was an approximate 40–50% tearing strength loss whether 2 or 8% resin add-on was obtained. This is probably due to cross-linking. Approximately 5–6% resin add-on gave a wrinkle recovery angle of 269°, with very little increase occurring at higher resin add-ons. The hand of the treated fabrics was good, but each of the treated fabrics was light yellow in color. This color prob-

lem as well as efficiency has been corrected, as shown below, with the use of a catalyst.

Since color was produced and the resin add-on was low in this treatment and since we had previously learned that the efficiency of APO when used with THPC was better than 80%, a screening of several catalysts was made, hoping to improve the efficiency.

TABLE I. The Influence of APO Concentration (Without Catalyst) Upon Resin Add-On, Tearing Strength, and Wrinkle Recovery

APO solids, %	Resin add-on, %	Tearing strength, Elmendorf, warp, g.	Wrinkle recovery (Monsanto), (W + F), degrees
8	1.9	600	236
12	3.8	530	240
16	4.7	510	266
20	6.0	510	269
24	6.6	480	270
28	7.6	500	277
Untreated control	—	1000	199

TABLE II. Catalyst Study for APO

Catalyst used	Solution pH	Resin add-on, %	Standard vertical char length, in.	Tearing strength, Elmendorf, warp, lb.
THPC	6.3	10.2	3.4	6.4
TEA*	9.7	6.6	3.5	7.3
$Zn(BF_4)_2$	6.8	14.0	2.9	5.7
$BF_3 \cdot C_2H_5NH_2$	7.1	12.9	3.3	6.8
$BF_3 \cdot DMF$	7.1	13.9	3.0	6.6
Catalyst AC	7.8	4.0	BEL†	—
None	6.4	4.2	BEL	9.2

* Triethanolamine.
† Burned entire length.

TABLE III. The Effect of Catalyst Concentration on Resin Add-On and Wrinkle Recovery

$Zn(BF_4)_2$ concentration	Solution pH	Resin add-on, %	Wrinkle recovery (W + F), degrees	Wrinkle recovery after Primenit VS treatment (W + F), degrees
1	6.2	9.0	270	278
2	5.9	10.0	281	290
4	6.0	11.7	285	301
6	5.9	13.6	289	303
8	5.8	12.1	289	307
10	5.8	13.6	286	307

Study of Various Catalysts for Use with APO

For this study a 25% solids APO solution was used and a catalyst concentration of 3%, based on the weight of APO, was tried. The fabric was 8.5-oz. O.D. Sateen. The same procedure as above was used in the treatment. It is shown in Table II that $Zn(BF_4)_2$ and the BF_3 complexes are more efficient catalysts.

It is interesting to note that with a resin add-on of only 6.6% an 8-oz. fabric would pass the standard vertical flame test with only a 3.5-in. char length, which is equivalent to the results obtained when APO-THPC is applied. It was necessary to make a further study on the most efficient catalyst in order to determine the most effective concentration to be used. A 15% solids APO solution was used; the catalyst concentration varied from 1% to 10% based on the weight of APO, using an 80 × 80 print cloth. Processing was the same as above. It is shown in Table III that resin add-on and wrinkle recovery angle increase with an increase in catalyst concentration up to about 4–6%, beyond which there is no improvement.

In view of this work, an experiment similar to that reported using APO alone was made in which 1% $ZN(BF_4)_2$, based on the weight of APO, was incorporated in the APO treating solution. As shown in Table IV, greater resin add-on was obtained with lower percent solids APO when the catalyst was used. Use of 12–16% APO solids gave a resin add-on of approximately 8% and adequate crease resistance.

The hand of all the samples was very good, and there was no change in the color of the fabric. Here again there was no noticeable difference in the tear-

TABLE IV. The Influence of APO Concentration Containing $Zn(BF_4)_2$ Catalyst Upon Resin Add-On, Tearing Strength, and Wrinkle Recovery

APO solids, %	Resin add-on, %	Tearing strength, Elmendorf, warp, g.	Wrinkle recovery (W + F), degrees	Wrinkle recovery (W + F), degrees, after 5 home launderings
8	2.9	600	253	245
12	6.2	600	272	278
16	8.1	580	282	285
20	10.5	570	285	286
24	12.9	580	295	290
28	15.0	570	298	303
Control	—	1000	199	206

ing strength of a sample containing 3% or 15% resin add-on, indicating that most of the tearing strength loss may be due to cross-linking.

Since additions of softener-lubricating agents to resin treated fabrics are known to improve the physical properties, a study was made on the influence of softeners on the wrinkle resistance, tearing strength, and other properties of APO treated fabric. The two softeners studied were octadecylethylene urea and polyethylene. It was found that the octadecylethylene urea, having the structural formula shown in Figure 6, gave superior results, especially when used as an aftertreatment. Since it contains an aziridinyl ring, it can react with cellulose in the same way as one of the aziridinyl rings in APO to produce a durable ether linkage with the cellulose. It is also possible for it to react with one of the hydrogens on the nitrogen resulting from the opening of one of the aziridinyl groups of APO. It was found that a concentration of approximately 1% Primenit VS (octadecylethylene urea) produced the best results, when used as an aftertreatment. When it was used in the APO formulation, results were not as good. The effect of a Primenit VS aftertreatment is shown in Table V. The samples shown in Tables I and IV were given a Primenit VS aftertreatment by padding through a 1% solution using 2 dips and 2 nips with a maximum squeeze roll pressure and then dried in an oven for 30 min. at 85° C., followed by a hot water rinse.

Use of the softener improves the wrinkle recovery angle (warp + fill) by approximately 30°, increases the Elmendorf tearing strength by approximately 80 g., and improves the hand. Resin add-ons of 6–8% produce wrinkle recovery angles greater than 300° with a loss in tearing strength of only 29%, after application of Primenit VS. Utilization of Primenit VS does not cause yellowing on heating. With a resin add-on of 15% and aftertreatment of Primenit VS, the crease angle was 319°, with a loss in tearing strength of only 38%. It is shown in Table V that an increase in resin add-on increases the crease resistance, the increase being much greater when Primenit VS is used. Many of the crease resistant resins reach a threshold value followed by a decrease in wrinkle resistance when the resin add-on exceeds the threshold value.

Influence of Home Laundering on the Properties of Fabric Treated with APO-Zn$(BF_4)_2$

The samples listed in Table V which were processed with APO-Zn$(BF_4)_2$ were given five home launderings with tumble drying. The results are shown in Table VI. Laundering does not affect the crease resistance of the samples treated with APO that were not given the Primenit VS aftertreatment, regardless of percent resin add-on, but there is an average loss of about 13° (W + F) after five home launderings in the samples treated with Primenit VS. This is probably due to the loss in Primenit VS, possibly due to the hydrolysis of Primenit VS before its application to the fabric, as it is not stable over

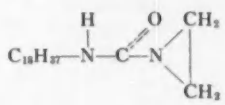

Fig. 6. Structural formula for octadecylethylene urea.

TABLE V. Influence of Octadecylethyleneurea Aftertreatment on the Properties of APO Treated Fabric

APO treated fabric					APO–Zn$(BF_4)_2$ treated fabric				
Resin add-on, %	Elmendorf tear, warp, g.		Wrinkle recovery (W + F), degrees		Resin add-on, %	Elmendorf tear, warp, g.		Wrinkle recovery (W + F), degrees	
	T	T + S	T	T + S		T	T + S	T	T + S
1.9	600	770	236	282	2.9	600	780	253	285
3.8	530	690	240	288	6.2	600	710	272	302
4.7	510	650	266	299	8.1	580	670	282	313
6.0	510	660	269	313	10.5	570	640	285	315
6.6	480	640	269	311	12.9	580	640	295	311
7.6	500	630	277	308	15.0	570	610	296	319
Control	1000	980	199	244	—	1000	980	199	244

T = treated; T + S = treated + softener.

long periods of time in emulsion form. The wrinkle resistance and retention, as well as muss resistance, were good in all of these samples.

Effect of Chlorine Bleach on APO-Zn$(BF_4)_2$ Treated Fabric

Chlorine retention tests were made on two different lots of 80 × 80 print cloth processed with APO-Zn$(BF_4)_2$, including the scorch test [1]. It is shown in Table VII that the fabrics have retained an average of 96% of their breaking strength after chlorine wash, and 86% after chlorine wash and scorch. The untreated fabrics retained 96% of their breaking strength after chlorine wash and 93% after chlorine wash plus scorch. This indicates that the amount of chlorine retention is low in comparison to values reported for many of the other nitrogen-containing wash and wear resins.

Effect of Aging of APO-Zn$(BF_4)_2$ Treating Solution on Ph, Resin Add-On, and Wrinkle Resistance

An APO treating solution containing 15% APO and 5% Zn$(BF_4)_2$ was used as standard. Samples were treated soon after the solution was prepared and each succeeding day for four days, using the same procedure as previously described. Solutions were aged at 26–28° C. and 9° C. It is shown in Table VIII that the solutions aged at room temperature changed in pH approximately 1.4 pH units in 4 days, but those aged at 9° changed less than 1 pH unit in the same period of time. The hand of the material was more crisp, and the fabric stiffened some as the solution aged. Resin add-ons are approximately constant, but the wrinkle resistance is lowered. However, fabrics treated with a solution of APO-Zn$(BF_4)_2$ which had been aged for 8 hr.

TABLE VI. The Influence of Laundering on the Durability of APO-Zn$(BF_4)_2$ Resin as Shown by Wrinkle Recovery Angle

Resin add-on, %	Wrinkle recovery angle (W + F), degrees			
	Before laundering		After 5 launderings	
	T	T + S	T	T + S
2.9	253	285	245	268
6.2	272	302	278	290
8.1	282	313	285	298
10.5	285	315	286	296
12.9	295	311	290	309
15.0	298	319	303	306
Control	199	244	206	—

TABLE VII. The Effect of Chlorine Bleach on APO-Zn$(BF_4)_2$ Treated 80 × 80 Cotton Print Cloth

Fabric	Resin add-on, %	Breaking strength strip, warp, lb.				
		Original	After chlorine wash	B.S. retained, %	After chlorine wash and scorch	B.S. retained, %
Lot 1						
Control	—	43.3	43.5	100	41.6	96.1
Treated	5.6	36.3	35.5	97.8	30.3	83.4
Lot 2						
Control	—	48.9	45.5	93.0	44.1	90.2
Treated	5.8	36.5	34.2	93.8	32.5	89.2

TABLE VIII. The Influence That Aging of APO-Zn$(BF_4)_2$ Solution Has on pH, Resin Add-On, and Wrinkle Recovery

Days of aging	Solution aged at 28° C.			Solution aged at 9° C.		
	pH	Resin add-on, %	Wrinkle recovery (W + F), degrees	pH	Resin add-on, %	Wrinkle recovery (W + F), degrees
0	6.2	12.9	317	—	—	—
1	7.2	11.0	302	7.1	—	—
2	7.4	10.9	279	6.8	—	—
3	7.5	10.7	263	6.4	—	—
4	7.6	11.2	254	7.0	11.8	311

had properties equivalent to those treated with fresh solution. Fabrics treated with APO-$Zn(BF_4)_2$ solutions that had been aged for 4 days at 9° C. had properties equivalent to those prepared from fresh solution.

Treatment of Various Type Fabrics with APO-$Zn(BF_4)_2$

Various fabrics as shown in Table IX were treated with a 15% solution of APO containing 1% $Zn(BF_4)_2$ based on the weight of APO, using the procedure already reported. It is shown in Table IX that APO-$Zn(BF_4)_2$ is effective in imparting wrinkle recovery to various fabrics. The hand and appearance of all of the fabrics were very good.

Wet Wrinkle Resistance Versus Dry Wrinkle Resistance

A sample of 80 × 80 cotton print cloth was processed with APO-$Zn(BF_4)_2$ to obtain a resin add-on of 9.4%. It is shown in Table X that the dry wrinkle recovery angle is greater than the wet wrinkle recovery angle by approximately 15% in the untreated control and 21% in the treated samples.

Crease Retention (Permanent Creasing)

Samples of 80 × 80 print cloth were wetted with an aqueous solution of APO-$Zn(BF_4)_2$ following the above procedures but were dried and cured as follows. Samples were ironed dry with a hand iron adjusted to the wool setting. Creases were ironed into the samples in the warp, fill, and bias directions. After drying, the samples were cured for 4 min. at 140° C. in a forced draft oven followed by the usual washing and drying process. The samples contained 5.8% resin add-on. These samples were given five home launderings, after which the creases were essentially unchanged. Samples of wetted fabric cannot be dried and cured with a hand iron adjusted to the cotton setting, since the intense heat has the tendency to decompose the resin, thus causing marked yellowing.

Abrasion Resistance

A sample of 80 × 80 cotton print cloth was treated with APO-$Zn(BF_4)_2$ to obtain a resin add-on of 9.8%. Samples of this fabric and the control were given 5, 10, and 15 home launderings. Abrasion resistance was determined after each series. The results are reported in Table XI.

It is shown in this table that the original abrasion resistance of the control fabric is much higher than the comparable resin treated sample, but after five home launderings the control value seems to fall to such a point that there is very little difference between the control and treated samples, the difference

TABLE IX. Effects of Treating Various Type Fabrics With APO-$Zn(BF_4)_2$

Type of fabric	Resin add-on, %	Wrinkle recovery (W + F), degrees	Tearing strength, Elmendorf (W + F), g.
8.2-oz. Cotton twill fabric	10.7	310	3650
2-oz. Cotton lawn fabric	10.4	307	810
140 × 64 Cotton broadcloth	6.3	280	1000
5.2-oz. Cotton poplin fabric	9.6	280	1960

TABLE X. Wet Wrinkle Resistance* Versus Dry Wrinkle Resistance

Fabric	Wet wrinkle recovery angle (W + F), degrees	Dry wrinkle recovery angle (W + F), degrees
Control	153	180
APO–$Zn(BF_4)_2$	249	317

* Wet wrinkle recovery angles were made using the Monsanto method, except that the fabric to be tested was wet out in water and blotted before making the test.

TABLE XI. Abrasion Resistance of APO-$Zn(BF_4)_2$ Treated 80 × 80 Cotton Fabric

Fabric	Resin add-on, %	Flex abrasion, Stoll: Original W	Original F	5× W	5× F	10× W	10× F	15× W	15× F
Control	—	1674	1315	273	234	161	189	170	122
APO–$Zn(BF_4)_2$	9.8	248	148	154	120	174	130	115	109

×—denotes the number of home launderings.

in the values possibly being within the experimental limits of the test. Some of the difference in the original values of the control and treated samples is possibly due to the fact that the treated samples had already undergone much washing in the application of the resin.

Fabric Properties

Durability

A sample of 80 × 80 print cloth containing 9.4% APO resin with 1.22% phosphorus and 1.74% nitrogen was boiled 3 hr. in a 0.5% soap solution containing 0.2% sodium carbonate. After the boil the fabric contained 1.22% phosphorus and 1.65% nitrogen. The wrinkle recovery angle was 268°, as compared to 278° before the boil. This loss in wrinkle recovery is probably due to some loss of the Primenit VS, as shown by no loss in phosphorus with a very slight loss in nitrogen content. Primenit VS on storage has limited stability. It is possible that hydrolysis had taken place before application to the fabric. This would result in additive finishing rather than chemical bonding.

The resin is also very resistant to home laundering. Table VI shows that an 80 × 80 print cloth with and without Primenit VS is stable to five home launderings. A sample of the 80 × 80 print cloth containing 9.8% resin, processed on the continuous basis and containing 1.50% phosphorus and 1.99% nitrogen, was subjected to 15 home launderings. Analysis after the launderings gave 1.55% phosphorus and 1.96% nitrogen, indicating a slight loss in nitrogen, probably also due to some loss of Primenit VS. The fabric had a wrinkle recovery angle of 291° after 15 home launderings as compared to 317° before the launderings.

An attempt was made to strip the APO resin from a treated sample using 1.5% phosphoric acid–5% urea solution at 80° C. for 30 min. without success. Attempts to hydrolyze the resin by treatment of the sample for 1 hr. in 0.1 *N* hydrochloric acid at 60° C., followed by thorough rinsing first in cold water and then in hot water, was likewise unsuccessful.

Strength

The strip breaking strength is reduced somewhat by the treatment. From values reported in Table VII, the samples with a Primenit VS aftertreatment lose approximately 20% of their breaking strength. It is known, however, that softeners lower the breaking strength while increasing the tearing strength. A complete study of breaking strengths has not been made. In our present work, the Elmendorf tearing test has been used to evaluate tearing strength retention. This new resin does reduce tearing strength, but not as much as is usually observed with other wrinkle resistant resins. It would appear that the strength retained should be adequate for most uses. There is a slight decrease in tear strength with increasing amounts of resin add-on, but this is not great in the range of 8–10% resin add-on, which is the amount necessary to impart good wrinkle resistance.

Hand and Appearance

The hand of the APO treated fabric is only slightly altered. It has a little fuller feel and is more resilient than the untreated fabric, due to the wrinkle resistance. The resin goes inside the fiber; therefore the feel is essentially that of the untreated fabric. Stiffness is one of the factors which influences hand. For comparison purposes a sample of APO treated sheeting containing 9.4% resin had a stiffness value of 4.5×10^{-4} in. lb. warpwise and 1.5×10^{-4} in. lb. fillwise as compared to the values of 5×10^{-4} and 2.5×10^{-4} in. lb. for the untreated control. These differences in stiffness values are all within experimental error. The appearance of the fabric is good even after 15 home launderings, followed by tumble drying.

Abrasion Resistance

Two methods were used to test abrasion resistance —the flex and flat methods. Probably neither method reflects actual use test, but a sample containing 9.8% resin had a flex abrasion (W + F) after 15 launderings of 224 cycles and 94 flat abrasion cycles as compared to 292 flex cycles and 79 flat cycles for the untreated control; see Table XI.

Chlorine Retention

Chlorine retention has been a fault of many of the nitrogen-containing wrinkle resistant resins being used at present. In order to have a wrinkle resistant resin-forming monomer that is generally useful, the resin formed should be resistant to chlorine bleaches. This seems to be a property in which APO resin treated fabrics is satisfactory. According to Table

VII, the amount of breaking strength retained by the resin treated sample when washed with a solution containing a chlorine bleach and then scorched was 86% as compared to 93% for the untreated fabric. The color of the fabric did not change when subjected to the chlorine bleach. A sample of APO-$Zn(BF_4)_2$ treated fabric containing 9.8% add-on was given a chlorine bleach after 15 home launderings. The fabric retained 95% of its breaking strength after the chlorine wash and scorch.

Flame Resistant Feature

In addition to APO imparting wrinkle resistance to cotton fabric, flame resistance is also an added feature which is dependent on the amount of resin added and also on the construction and weight of the fabric. As shown in Table II, an 8.2-oz. twill containing only 6.6% resin add-on would pass the standard vertical flame test with less than a 4-in. char length. An 80 × 80 print cloth would require approximately 18% resin add-on to pass the standard vertical flame test. However, lesser amounts will change the burning characteristics of the fabric, and in each case leave a tough black ash which may offer some protection to the individual.

Air Permeability and Rate of Drying

A sample of 80 × 80 print cloth containing 9.4% resin add-on had an air permeability of 54 $ft.^3/min./ft.^2$ as compared to 87 $ft.^3/min./ft.^2$ for the control. The resin treated sample dried at a faster rate than the control.

Dimensional Stability

Cellulose fibers shrink largely because of swelling. As a general rule there are three chemical methods by which shrinkage can be reduced in cellulosic fibers: (1) use of a surface resin to form a sheath bonded to the surface of the fiber, (2) use of internal resin to fill fiber interstices, and (3) use of cellulose reactant to cross-link the molecule. APO treatment of cotton reduces shrinkage according to (2) and (3) above. When the dimensional stability was checked by thread count before and after treatment and laundering, there was less than 2% shrinkage.

Processing of Fabric

There are additional details that must be studied before the best method of applying APO to fabric will be known. Consequently, we have tentatively adopted the following procedure for processing based upon experimental data and experience with other resin finishes. When changing from small laboratory equipment to pilot plant equipment it was necessary to increase the catalyst concentration to 5% in order to duplicate the laboratory scale results. This is probably due to inadequate curing, since the oven used was the steam heated type and the highest attainable temperature was lower than 140° C.

Procedure Used on Pilot Plant Equipment Run

The treating solution was made by dissolving 450 g. APO, 30 g. Triton X-100, and 56.3 g. of a 40% $Zn(BF_4)_2$ solution in 2464 g. water, the catalyst being added last. The temperature of the solution was 30–35° C. and the pH was 5.7. The concentration of the APO was 15%. Fifteen yards of full width 80 × 80 cotton print cloth was padded through the solution using two dips and two nips. The wet pickup was 86%. The wet fabric was dried immediately for 4 min. at 85° C. and then cured for 4 min. at about 140° C. The fabric was washed in a winch for 5 min. in cold water followed by 30 min. in hot water at 140° F. The last hot wash contained 0.01% Igepon T. This was followed by a 5-min. wash in hot water and a 5-min. wash in cold water. After being dried in an oven at 110° C., the fabric was softened by padding through a 1% solution of Primenit VS using 2 dips and 2 nips with maximum squeeze roll pressure and dried for 30 min. at 85° C., followed by a hot water rinse and drying again. The fabric contained 9.8% resin.

Summary

Cotton fabrics have been made crease resistant by processing with tris(1-aziridinyl)phosphine oxide, a new resin-forming monomer, called APO. Fabrics were treated by padding them through an aqueous solution of the resin-forming monomer containing $Zn(BF_4)_2$, then drying and curing at an elevated temperature to form an ether linkage with the cellulose and also to form an insoluble resin inside of the fibers.

The new crease resistant resins have the following features:

1. Treating solutions are sufficiently stable.
2. The amount of resin necessary to impart crease resistance is comparable to other crease resistant resins.

3. The resin treatment alters the hand of the fabrics only slightly.

4. The tear and tensile strengths of the treated fabrics are better than those obtained with most crease resistant resins.

5. The strength of the treated fabrics is not damaged greatly by chlorine bleach.

6. The resin is very resistant to neutral, alkaline, and acid washes.

7. The resin has the feature of imparting some flame resistance as well as crease resistance.

8. The resin imparts permanent creases to cotton garments.

All of the experiments reported here are preliminary and have served to select a set of processing conditions which are not necessarily the optimum. Additional experiments are being conducted in order to gain the necessary information which will be used to establish the conditions which will produce wrinkle resistant fabrics with the best possible properties.

Acknowledgment

The authors wish to express their thanks to Margarette Louglin, Julia M. Sloan and Janice P. Evans for the textile testing, to Julian Jurgens for nitrogen analyses, to James A. Harris for phosphorus analyses, and to Rita M. Perkins for the home launderings reported in this paper.

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Bleaching of Cottons in Home Laundering[1]

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Introduction

Regular bleaching of cottons in home laundering has become common practice in millions of American homes. Of the various types of products commonly used with soaps and detergents in the laundry, bleach is by far the most widely used and accepted. The extent to which bleach is being used throughout this country can best be illustrated by some unpublished figures taken from several recent studies of bleach usage habits in home laundering. These scientifically designed studies covered interviews with thousands of housewives from all parts of the country.

There are approximately 50 million family units in the U. S. today, and the family wash, at least in part, is machine laundered at home in about 90% of these units. Within this group doing laundry at home, bleach is used regularly by about eight housewives out of ten (Figure 1). Such broad usage of bleach certainly suggests that housewives feel a very definite need for bleach as a part of a thorough, well balanced laundering procedure.

Bleach Types

Before discussing bleach usage habits, perhaps a quick review of types of bleaching materials available to consumers would be in order.

Bleaches break down broadly into two chemical categories—the peroxy type bleaches and the active chlorine-containing bleaches. The peroxy type bleaches are represented by hydrogen peroxide, sodium perborate, and other peroxy compounds, including the newer sodium monopersulfate. In general, the peroxy bleaches have been regarded as "fine fabric" or "light duty" bleaches by consumers, and even sodium perborate, the most widely used bleach of this type to date, has never been an important factor in the "heavy duty" laundry bleach field. The peroxy type bleaches are essentially foolproof to use —i.e., the consumer runs essentially no risk of damaging fabrics or running into complications with resin-finished goods when using peroxy bleaches, even if she uses them improperly. However, they are not a match for the chlorine-containing bleaches in bleaching effectiveness, and it is believed that this disadvantage has been responsible for their relatively slow market growth in this country. On the other hand, peroxy bleaches have been very popular for many years in Europe, where greatly improved bleaching efficiency is achieved due to the practice of boiling clothes in the wash water.

The chlorine-containing bleaches are of several types. The liquid bleaches commonly used today are sodium hypochlorite solutions, made by the direct chlorination of dilute caustic soda solution. There have been many different liquid bleach brands available over the years, most of this tonnage being sold at a labeled strength of 5.25% sodium hypochlorite. Liquid sodium hypochlorite bleaches are generally regarded as the most effective bleaching agents available and the least expensive to use. No other form of bleach has yet seriously challenged the strong market position of liquid hypochlorite.

Incidentally, liquid potassium hypochlorite and granular lithium and calcium hypochlorites are well known, and the latter is widely available commercially. All bleach as effectively as sodium hypochlorite on an equal available chlorine basis, but

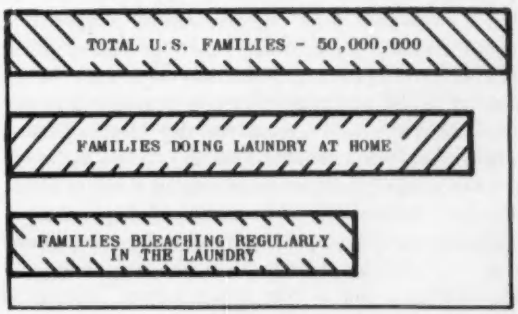

Fig. 1. General experience with bleach.

[1] Presented at the Chemical Finishing Conference of the National Cotton Council, Washington, D. C., October 1, 1958.

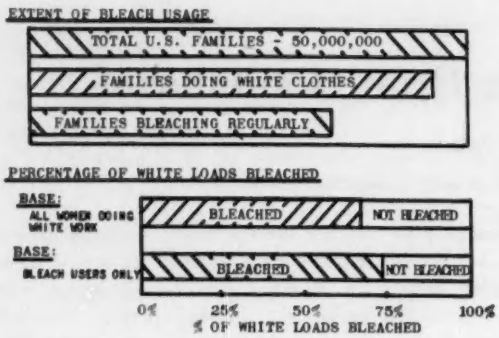

Fig. 2. Bleaching of white cottons.

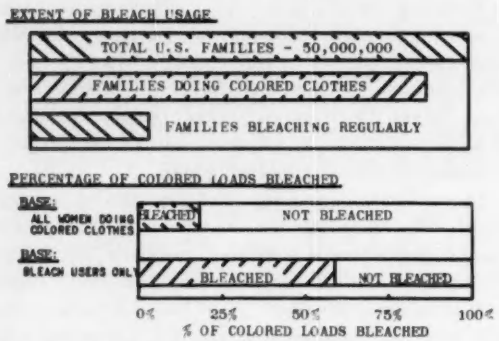

Fig. 3. Bleaching of colored cottons.

none have yet been able to compete effectively with sodium hypochlorite either because of cost reasons or inadequacies in other product characteristics or areas of performance. Consequently, none have ever been sold successfully in large quantities for home laundering.

More recently, the granular organic chlorine-containing bleaches have received considerable attention. Dichlorodimethylhydantoin has been used as the bleaching agent in a number of dry bleach brands, but its cost and level of effectiveness compared to liquid sodium hypochlorite have prevented these brands from becoming prominent in today's bleach market. The chlorine-containing cyanuric acid derivatives are now entering the dry bleach picture. These can be formulated into dry products which are about equal in effectiveness on an equal available chlorine basis with the inorganic hypochlorites. They also offer the opportunity to make a dry bleach that is safer for fabrics than the dry inorganic hypochlorites, but a cost disadvantage relative to liquid hypochlorite bleaches still exists at the present

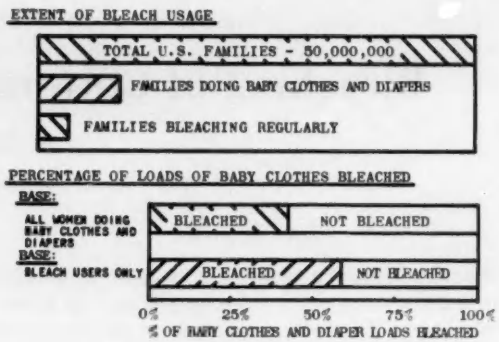

Fig. 4. Bleaching of diapers and baby clothes.

time. It remains for the consumer to decide if a dry bleach is worth a premium price.

At present, about nine out of ten consumer dollars are being spent for the liquid sodium hypochlorite bleaches, with the remaining dollar going for the various types of dry powdered bleaches formulated in a variety of ways. Because liquid bleaches are being used so extensively, the remainder of this discussion will be concerned primarily with this type of bleach.

Bleach Usage Patterns

It is estimated that the current liquid bleach market is over 600 million quarts of bleach per year, or roughly 14 quarts per family. Let's take a look at how and for what laundering purposes this quantity of bleach is used each year. Again, we draw upon the results of actual interviews with consumers for our figures.

Regular laundry accounts for the major share of this bleach volume. Taking a look first at white clothes in the laundry (Figure 2), we note that of those women who do white clothes at home, almost 80% use bleach with regularity. In terms of loads of white clothes laundered, about seven out of every ten loads are given bleach treatment. We should mention here that about half of the total housewives doing white work at home claim to use bleach on *every load* of white clothes.

Bleach is used on colored clothes less frequently than on whites (Figure 3). Of those housewives who launder colors at home, about 30% claim to use bleach on colors, as compared with about 80% on whites. Bleach is used in about one load in five of all colored clothes, although women in the habit of using bleach on colors tend to use it almost with as

much regularity as they do on whites—about 60% of all colored loads that this group launders are laundered with bleach. These figures indicate that while bleach usage on colors is appreciably less than on whites, a significant quantity of colored material is still being given the soil and stain removal benefits of bleach each year to the satisfaction of many American housewives.

Baby clothes and diapers constitute another important area of bleach usage (Figure 4). Approximately 20% of the housewives in the country are concerned with the problems of laundering baby garments, and the percentage of this group using bleach regularly is a substantial 40%. Frequency of bleach usage is about one out of every two washer loads of these items.

Subjective comments on the amount of bleach housewives use per load indicate that they generally use an amount equal to, or slightly less than, the ½ oz. of bleach per gallon of water recommended by most bleach manufacturers. Ninety percent of those housewives using bleach report using one cup (8 oz.) or less per load, while 35% report using a half cup or less. It should be pointed out, however, that only about one-third of these housewives using bleach actually claim to measure product with regularity, so these usage figures may be subject to question.

Although most bleach manufacturers point out that equally satisfactory bleaching can be done in the wash, the rinse, or in a pre-wash soak, most bleach users—about 70%—choose to do their bleaching in the wash. The remaining 30% is split between bleaching in a pre-wash soak and bleaching in the rinse. It's likely that as automatic washer saturation increases, the percentage of housewives using bleach in the wash will become even higher.

Bleach usage patterns show almost no variation with geographical location, economic class, or water hardness. However, age of the housewife does make a difference. In general, the percentage of housewives using bleach is greater among younger women than among older women. In addition, younger women use bleach more frequently, probably because the average age of their children is much lower and the problems they face in the laundry demand a more thorough, better balanced laundering procedure which includes bleach. It is interesting to note that bleaching is definitely *not* a practice just of older housewives. Bleach is being used as frequently now as it was ten years ago, and it will probably be used as frequently ten years from now as it is today.

Consumers' Attitude Toward Bleach

Housewives give a number of reasons for using bleach regularly. They talk primarily in terms of the improvement it makes in the appearance of their laundry, mentioning that bleach helps get clothes clean, aids in whitening grayed fabrics, and removes stains. They also mention liking the fresh odor they feel bleach imparts to clothes, and they recognize and appreciate the fact that bleach has important disinfecting properties.

We know from direct questioning that over 60% of housewives using bleach are aware that bleach can seriously weaken cotton if handled carelessly. Despite this recognition of the damage potential of liquid bleaches, very few housewives expressed concern over this product characteristic or viewed it as a product negative. It is certainly apparent that most women feel the advantages of using bleach more than justify the attention required to use it properly.

Liquid hypochlorite bleach is, of course, chemically very active. Its effectiveness as an oxidizing bleaching agent hinges on this activity. It is reasonable then that consumers who use bleach improperly can be expected to encounter trouble. For example, when damage does occur to cotton in the home laundry, it's very likely that it was caused when undiluted bleach was accidentally spilled on dry clothes.

Damage also results sometimes when undiluted bleach is poured directly into a washer after the clothes have been added. If for any one of several reasons there should happen to be only limited agitation in the tub, then sizable areas of fabric may be exposed to highly concentrated bleach for several minutes. Whenever undiluted or highly concentrated bleach and cotton are permitted to come into contact in this manner, the result is inevitably the formation of oxycellulose and the subsequent deterioration of the garment with repeated washings and wearings. Because of the high oxidation potential of undiluted bleach, most bleach manufacturers emphasize that bleach should not come into contact with clothes in undiluted form.

As we pointed out earlier, housewives are apparently quite conscious of the fact that careless use

of bleach can lead to fabric damage. Generally, when damage of this type occurs, most consumers tend to blame themselves for the damage because of their careless handling of the bleach. Only an occasional housewife feels that she has been misled about the safety of bleach for cotton when damage of this type accidentally occurs.

Consumer Problems With Bleach and Chlorine-Retentive Finishes

At the present time, the amount of consumer correspondence we are receiving relating to accidental fabric damage is insignificant compared to the amount we are receiving on damage or discoloration due to the retention of chlorine by certain fabric finishes. The following is what we see of the problem as bleach manufacturers—the types of garments which seem to be causing the greatest difficulty, the nature of the damage, and the magnitude of the problem as indicated by our consumer correspondence.

From August 31, 1957 to August 31, 1958, almost 400 consumers have written to us about problems clearly related to retention of chlorine by resin fabric finishes. This number may sound relatively insignificant, but The Clorox Company is only one

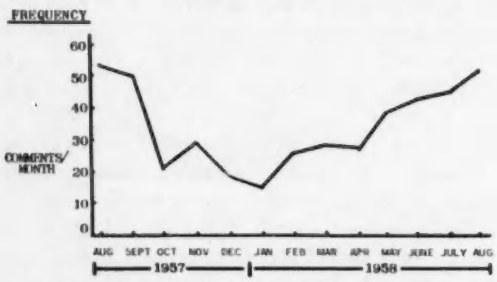

Fig. 5. Consumer comments relating to chlorine retention—August 1957 through August 1958.

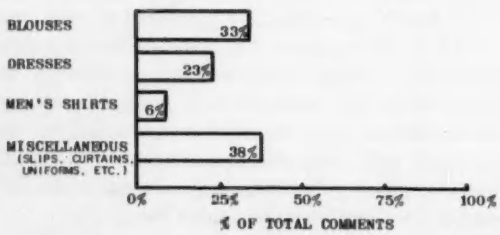

Fig. 6. Consumer comments relating to chlorine retention by garment type—August 1957 through August 1958.

of many bleach manufacturers, and our correspondence does not reflect any of the problems which commercial laundry people are seeing. In addition, for every person who takes the time to write a letter for assistance, there are usually many more who encounter the same problem but who choose not to write for one reason or another.

As we look at these comments on a monthly basis over this period, a clear-cut pattern develops centering around an August–September peak and a December–January low (Figure 5). This would seem to correlate fairly well with the times of year when the present types of resin-treated goods are being worn to the greatest and least extent.

A breakdown of these totals shows that the garment types with which consumers had the most difficulty were ladies' dresses and blouses (Figure 6). Blouses constituted 33% of the total, dresses another 23%. Only 6% of these comments were on men's shirts, which we feel indicates what a good job manufacturers of that particular type of garment have done toward eliminating consumer difficulties of this type. The remaining 38% were on miscellaneous items, such as uniforms, slips, kitchen curtains, etc.

Almost all of these comments relate to the distinctive fabric yellowing which normally takes place when bleach treatment is given a garment finished with melamine formaldehyde. Fortunately, most garments which have undergone this change can be easily restored to their original color and, although the garment will still be as sensitive to bleaching as it was before, at least it is still usable. Perhaps our choice of words in saying the original color can be "easily restored" is not too good. It's certainly easy for textile scientists to do, since they can recognize the nature of the problem and have ready access to sodium hydrosulfite or some other effective reducing antichlor. But how many women even know what makes cotton wash-and-wear the easy-to-care-for fabric that it is? How many would know what to do about a yellowing problem that, in their minds, is caused by the bleach that they normally would expect to help them with such a problem? We suspect that very few women do. For any woman lacking the proper know-how, the problem is *not* an easy one to solve.

The number of comments we receive on fabric damage relating to chlorine retention by urea-formaldehyde type resins, as best we can judge by the

fabrics, is admittedly not high. However, we do not feel it would be sound to conclude that this type of damage is no longer a consumer problem in home laundering. Whereas the yellowing of a single article in an all-white wash is distinctive and puzzling to the housewife, the deterioration of fabrics treated with urea-formaldehyde types of resin which have been bleached and ironed is not unlike what most women would expect if they had accidentally spilled undiluted bleach on the fabric at some stage of the washing process. As we mentioned earlier, in such cases, many housewives assume they've been careless in handling bleach, and they blame themselves for the damage without recognizing its true nature. It's understandable that not too many women think to take their problem to the bleach manufacturer. The unfortunate thing about this type of damage, of course, is that there is little anyone can do for the consumer once the damage is done.

Conclusions

This then is what we know of the home laundry bleaching habits of the American housewife—the types of bleach she uses, the way she uses them, what she likes and dislikes about them, and the problems she has with them. In summing up, there are several points in particular that we would like to emphasize:

1. The average American housewife is a regular or near-regular user of liquid hypochlorite bleach. The extent to which she uses bleach indicates that she feels a very definite need for bleach as a part of a thorough, well balanced laundering procedure.

2. Cottons which are white or even partially white in color will almost inevitably be laundered with bleach at some time during their lifetime. Colored cottons are certainly not being laundered with bleach today with the regularity of whites, but there are definite indications that the volume of colored goods on which bleach is being used regularly to the satisfaction of both the housewife and the textile manufacturer is steadily increasing.

3. Wash-and-wear cotton garments of the types and colors which the housewife normally thinks of bleaching—e.g., shirts, sheets, and blouses in white or pastel shades—are almost certain to be bleached with the frequency of their unfinished counterparts, regardless of label or hang tag instructions.

This information clearly suggests that any wash-and-wear cotton manufacturer interested in selecting the proper finish for his garments or fabrics should give very careful consideration to the likelihood of his goods eventually being given bleach treatment in the home laundry. The odds are too much in favor of any white and many colored wash-and-wear garments being laundered with bleach for the manufacturer to neglect this consideration if he wishes to give full value and full satisfaction to the consumer. If any question exists regarding the likelihood of a particular garment type eventually being bleached, the odds certainly support the selection of a safe, bleachable finish if consumer problems are to be kept to a minimum.

There are certainly indications that more and more bleachable finishes are being used or will be used in the near future in the manufacture of wash-and-wear cotton garments. This is extremely encouraging. It would seem that the use of such finishes represents the only satisfactory approach to solving the problem the consumer faces in trying to do the most efficient job possible in laundering both her regular laundry and her new resin-treated cotton garments and fabrics.

Triazones—Creaseproofing Agents for Cotton[1]

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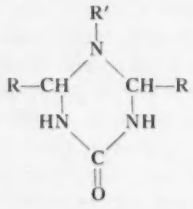
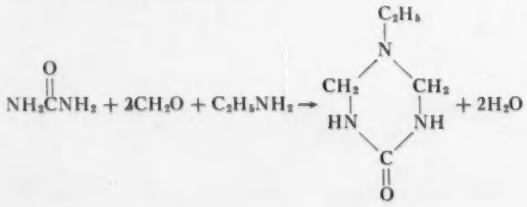
Abstract

The triazones have been known for a long time as chemical compounds, but have only recently come into prominence as creaseproofing agents. Fabrics treated with pure triazone resins show no damage due to retained chlorine and, when triazone resins are mixed with resins normally exhibiting high damage due to retained chlorine, they exert a chlorine damage depressant effect. Triazone resin finishes compare favorably with the best of the nitrogenous resin finishes in respect to durability and crease resistance–fabric strength relationships. Fabrics treated with some triazone resins show some tendency to discolor at elevated temperatures, but this discoloration can be easily removed. Although the triazone resins have been blamed for imparting odor to fabrics, this has not been a problem in commercial usage where properly prepared resins and proper treating conditions have been employed. The triazone resins have now been used commercially on a large scale and have been found to be a valuable addition to the finisher's line of creaseproofing materials.

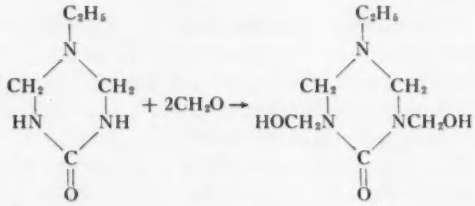
THE COMPOUNDS which have become known in the textile industry as "triazones" are more properly called tetrahydro-s-triazin-2(1H)-ones and have the following structural formula:



The R and R′ groups may be hydrogen, alkyl groups, or substituted alkyl groups. The triazones are conveniently prepared by the reaction of urea, an aldehyde, and ammonia or a primary amine. In the case of 5-ethyl tetrahydro-2(1)-s-triazone, which is the compound most often encountered in the textile industry, the reactants are urea, formaldehyde, and ethylamine, and the reaction takes place according to the following equation:



The compounds actually used as creaseproofing agents are dimethylol triazones, which are produced by reacting the triazones with two moles of formaldehyde under alkaline conditions; they may be prepared in one step by the reaction of the amine, urea, and four moles of formaldehyde.



Although the triazones have only recently come into prominence as creaseproofing agents on a commercial scale, they have been known for a long time. As far back as 1892, Dixon [4] was studying the reaction leading to triazones, although the products obtained were not recognized as being cyclic at that time. In 1935, Steindorf and Pacquin [9] described methods of manufacture for a wide variety of triazones and claimed that these compounds were "valuable assistants in the textile industry." In 1943, Burke [2] described the methyl ethers of di-

[1] Presented at the Chemical Finishing Conference, National Cotton Council of America, Washington 6, D. C., October 2, 1958.

methylol triazones as useful for treating cellulosic fabrics to reduce shrinkage and improve resilience. Apparently no appreciable commercial use of the triazone resins for treating textiles was made in this country, however, until the early 1950's, when at least two triazone resins appeared on the American market and were used commercially to a somewhat limited extent. These early resins were what we will call "straight" triazone resins, that is, resins containing only dimethylol triazones as the active crease-proofing agent. They did not enjoy widespread use, probably because of certain weaknesses which they possessed—low effectiveness, discoloration at high temperatures, and comparatively high cost. Research workers attempting to improve these early resins discovered the surprising fact that, in mixtures with urea formaldehyde, the triazone resins eliminated damage from retained chlorine on treated fabrics. It was also found that triazones, when mixed with any resins exhibiting high damage due to retained chlorine upon application to fabrics, would similarly exhibit a "chlorine damage depressant" effect. This discovery, now the subject of pending patent applications, made possible resins containing up to fifty mole percent of urea formaldehyde resin or other highly chlorine retentive resins which show no damage due to retained chlorine when applied to fabrics.[2] These mixed resins are cheaper, more effective, and show less discoloration at high temperatures than the straight triazone resins. When these mixed triazone resins began to find considerable usage in the industry, many similar resins were introduced, so that now there are on the market a number of triazone resins. These resins vary in solids content from less than 50% to over 80%, in shelf life from a few weeks to many months, in triazone-to-urea formaldehyde mole ratio from less than one-to-one to infinity, and in free formaldehyde content from almost none to very large excesses. Thus the problem of dealing with the triazone resins today is far different from that which confronts us in dealing with resins such as the cyclic ethyleneurea resins where, although there are many manufacturers and suppliers, in general the resins are all very similar.

If paper chromatograms are run on the various types of triazone resins which are on the market using a 3:1:1 butanol:ethanol:water mixture as the developer and detecting the spots by spraying the paper with an acid catalyst, curing, and dyeing with an acid dye [6], differences in these resins are readily apparent. Dimethylol-5-ethyltetrahydro-2-(1)-s-triazone prepared from 5-ethyltetrahydro-2(1)-s-triazone which has been carefully purified by recrystallization gives only one spot at $R_f \cong 0.65$, and the 5-hydroxyethyl compound, which is found in at least one commercial product, gives a spot at $R_f \cong 0.57$. In addition to the dimethylol triazone spot, most of the so-called straight triazone resins contain an additional spot just above the dimethylol triazone spot, although in some of the newer resins of this type which are claimed by their manufacturers to be cleaned up, this spot is absent. In the mixed triazone resins the unknown spot above the dimethylol triazone spot is usually absent, but there is present a spot corresponding to dimethylol urea at $R_f \cong 0.45$. In addition to the dimethylol urea and the dimethylol triazone spots, the mixed resins sometimes contain polymer spots or streaks below the dimethylol urea spot. In cases where the resins are unstable, in running chromatograms from time to time over a period of several weeks the dimethylol spots will be seen to become weaker while the polymer spots become stronger and lower in R_f value.

TABLE I

	Crease resistance*	Filling tear†	Filling tensile‡	Reflectance after curing**
Resin A	258	1.84	43.0	85.8
Resin B	253	1.97	47.1	82.1
Resin C	243	2.03	47.7	84.4
Resin D	216	2.30	52.2	83.9
Resin E	244	2.02	48.1	86.9
Resin F	226	2.35	50.1	80.6

* Monsanto—warp and filling.
† Trapezoid.
‡ Scott Tester.
** Photovolt Reflectometer, blue filter.

As an illustration of how different various triazone resins are, six commercially available products were applied to samples of 80 × 80 print cloth using the same resin and catalyst concentrations and the same curing conditions with the results shown in Table I.

All samples were treated with 15% resin and 3% of a metal salt–organic acid catalyst and cured for 70 sec. at 165° C. Note that Resins B and F,

[2] The basic work in the field of mixed triazone resins was done by George S. Y. Poon, formerly of the Research Division of Dan River Mills and now with Standard Chemical Products Co.

which are straight triazone resins, discolor the fabric considerably on curing. Resin C, which is a cleaned-up resin, shows less discoloration on curing. Resin D is a mixed resin containing a high percentage of triazone resin. This resin is unstable on storage and has reduced effectiveness due to polymerization. Both Resins A and E are resins containing near the maximum amount of urea formaldehyde resin possible in order for chlorine damage to remain low. Resin A contains considerable free formaldehyde, which is evidenced by high crease resistance but low strength properties. All the products are satisfactory from the standpoint of exhibiting low chlorine damage when applied to fabrics.

In dealing with the triazone resins in this paper, no further attempt will be made to compare the various such resins on the market. To simplify presentation, one straight and one mixed triazone resin have been chosen from among the better triazone resins on the market, and fabric properties which can be expected from these resins as compared with those expected from other types of creaseproofing agents will be discussed.

The primary reason for applying triazone resins or any resins to cotton fabrics is to improve the crease resistance of the fabric and/or to stabilize the fabric to shrinkage on laundering. Usually any finish which is sufficient to give high crease resistance will simultaneously give shrinkage control. Whenever high crease resistance is obtained by resin treatment, there is obtained concurrently a decrease in the tear, tensile, and abrasion strength of the fabric. As has been pointed out by Foster [5], Cooke and coworkers [3], Stam and coworkers [8], and others, the relationship between crease resistance and fabric strength is affected by many factors such as amounts of resin, curing times and temperatures, catalyst concentrations, etc. as well as by the nature of the resin. In general, high resin concentrations, low catalyst concentration, and mild curing conditions are conducive to the best crease resistance–strength relationships; however, these conditions are not consistent with the most economical usage of creaseproofing materials. In the case of the cyclic ethyleneurea resins, they do not lead to minimum chlorine retention, since these resins need a hard

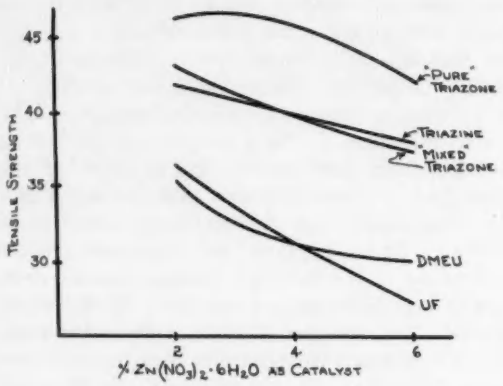


Fig. 1.

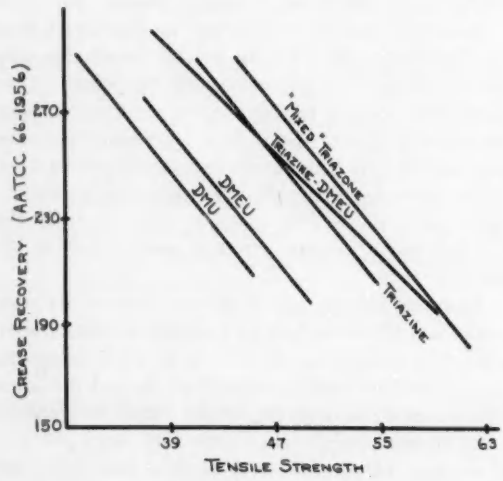


Fig. 2.

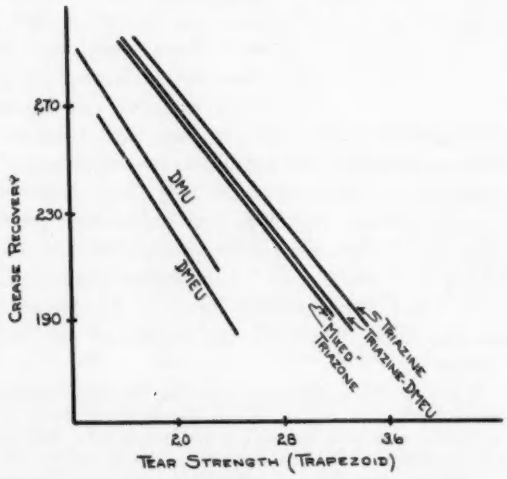


Fig. 3.

cure in order to have the lowest possible chlorine retention. With the straight triazone resins and those mixed triazone resins which do not contain too high a percentage of urea formaldehyde, a hard cure is not necessary for low chlorine retention; therefore, they may be used under conditions conducive to good crease resistance–strength relationships if desired. On the other hand, many finishers wish to use the most severe conditions of cure possible in order to obtain the maximum effectiveness from the creaseproofing agents being used. When the non-nitrogenous creaseproofing agents and the nonbasic nitrogenous resins such as dimethylol ethyleneurea and dimethylol urea are used under conditions of maximum effectiveness, very careful control of treating conditions must be maintained to avoid excessive loss of strength of the fabric being treated. Any variations in the alkalinity of the fabric, catalyst concentration, or curing conditions can cause considerable variation in the strength of the finished fabric. The triazone resins and the triazine resins, however, are much less sensitive to treating conditions and can be employed under conditions of maximum effectiveness with less danger of excessive fabric damage. This difference in the sensitivity of the various resin types to overcuring may be illustrated by Figure 1, which shows the variations which are obtained in tear strength of fabrics treated with various resins as the amount of catalyst is increased above that needed for catalysis of the resin. In this case the catalyst used was zinc nitrate. The curing was held constant at 330° F. for 70 sec., and the resin concentration was held constant at 6.0% solids on the fabric.

Cooke and coworkers [3] and Stam and coworkers [8] have already pointed out that better crease resistance–strength relationships can be expected from the triazine resins than from the cyclic ureas. When the more common types of nitrogenous creaseproofing agents are compared under identical treating conditions, it is found that the triazones compare favorably with the triazines in crease resistance–strength relationship and are superior to the dimethylol cyclic ureas and dimethylol urea. The urea formaldehyde resins generally used commercially contain only 1.3–1.6 moles of formaldehyde per mole of urea rather than 2. These commercial resins generally show better crease resistance–strength relationships than dimethylol urea but are less effective and less durable. Figure 2 shows the crease resistance–tensile strength relationships obtained when samples of 80 × 80 print cloth were treated with varying percentages of various types of resins, using 12.5% of zinc nitrate hexahydrate based on the wet weight of the resin as catalyst and curing for 70 sec. at 330° F. The different points on the curves represent different resin concentrations. Note that the triazones and triazines retain their superior crease resistance–strength relationship even when mixed with other resins.

Figure 3 shows the crease resistance–tear strength relationships obtained on the same set of samples as in Figure 2. Note that similar relationships are found with tear strength as with tensile strength.

In general, the non-nitrogenous creaseproofing agents show poorer crease resistance–strength relationships than do the nitrogenous resins. Although an extensive comparison of the non-nitrogenous creaseproofing agents with the triazone resins is beyond the scope of this paper, Table II shows some

TABLE II. 80 × 80 Print Cloth

Type finish	Crease resistance*	Filling tear*	Filling tensile*	Reflectance after curing*
A—Dialdehyde	242	1.97	44.1	71.8
B—Epoxy	223	1.93	40.6	86.5
C—Epoxy + DMEU	244	1.92	41.1	86.4
D—Acrolein-formaldehyde resin	236	1.65	39.5	82.8
E—Ketone-aldehyde resin	188	2.34	43.9	41.3
F—Acetal	204	2.61	50.7	86.8
G—Mixed triazone resin	231	2.65	47.2	86.6
H—Caustic-halohydrin	154†	3.23	54.0	—
I—Wet C.R. finish (Expt'l)	146‡	3.85	50.0	—

* For method of measurement see Table I.
† Wet crease resistance—223.
‡ Wet crease resistance—280.

of the typical fabric properties obtained with these materials as compared with those obtained with a mixed triazone resin.

In each case the creaseproofing agent was applied in a formulation recommended as being best for that particular material by the supplier; or, where suppliers recommendations were unavailable, formulations were used which previous experience had shown to be best for the given materials.

The triazone resins, because they are basic, present a problem in catalysis, since they tend to buffer catalysts and make maximum effectiveness hard to achieve. Almost all of the common catalysts used with other resins have been used with the triazone resins, although metal salts, organic acids, and metal salts in combination with organic or inorganic acids have been favored.

The mixed triazones present another problem—that of the storage stability of the urea formaldehyde component. Excess formaldehyde in the resin improves stability but increases odor and hurts the crease resistance–strength relationship.

Some manufacturers of mixed triazone resins have had difficulty in obtaining storage stability due to the urea formaldehyde component; however, there are stable mixed triazone resins on the market having low odor and excellent crease resistance–strength relationships.

The straight triazone resins appear to have relatively low effectiveness as creaseproofing agents or, stated in another way, their reactivity with cellulose is low. When the triazones are mixed with urea formaldehyde resins, the effectiveness of the mixture is much greater than that of the pure triazone resins. The two components of the mixture apparently do not react independently of each other; thus the mixed triazone resins are not a mere mixture of resins but a new composition of matter with properties differing from those of either of the components. Figure 4 shows the percentage of strength lost when a treated fabric was padded with 33.3% sulfuric acid and allowed to hang in the air for 5 hr. versus the mole percent of triazone applied to the fabric and cured under constant curing conditions. It is interesting to note the ability of the triazones to protect the fabric from acid damage, even when the acid is in excess of the stoichiometric amount necessary to neutralize all of the triazone applied to the fabric. If we assume that the degree of protection from acid damage is proportional to the amount of triazone fixed on the fabric, then it can be seen that more triazone is fixed when mixed with urea formaldehyde than when applied alone, indicating coreaction of the two materials. Chromatographic studies also indicate that triazone and urea formaldehyde resins copolymerize, because when a mixture of the two materials is warmed under acidic conditions both the dimethylol urea and the dimethylol triazone spots disappear, although when the dimethylol triazone alone is treated under the same conditions its spot remains.

In discussing the property of fabrics known as chlorine retention, it may be helpful to define certain terms normally used in describing this phenomenon and review briefly some of the chemical reactions involved. Nuessle [7] has already done this to a large extent in a recent article, but perhaps some of his points can bear repetition here. Chlorine retention may be defined as the phenomenon of chloroamide formation by the action of hypochlorite solutions on fabrics containing fixed nitrogenous materials. Chlorine damage may be defined as the loss of fabric strength which occurs when a fabric containing chloroamides is subjected to elevated temperatures, and is normally measured by the AATCC Tentative Test Method 69-1952. As far as the utility of a fabric is concerned, chlorine retention is of little importance as long as there is no chlorine damage. Fabric bases may be defined as any materials of measurable alkalinity which are fixed to the fabric or which are present during the scorching step

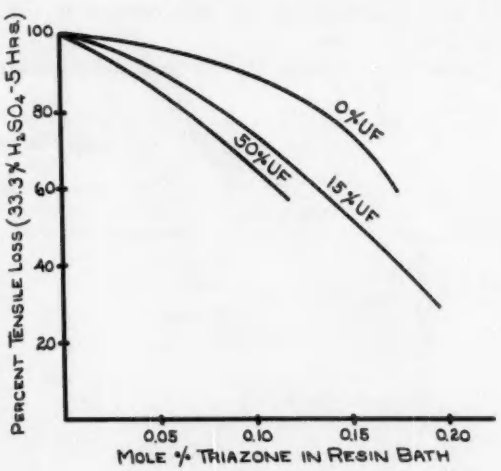


Fig. 4.

of the AATCC test. These bases may be inorganic bases such as sodium hydroxide or magnesium hydroxide, sodium carboxymethyl groups on the fabric, or resins which have been fixed on the fabric. A chlorine damage depressant may be defined as any material which, when added to a finish which normally shows high chlorine damage when applied to fabric, will reduce chlorine damage.

With the preceding definitions in mind, the chemical reactions involved in the phenomenon of chlorine retention and chlorine damage may be schematically represented as follows:

A) $OCl^- + H^+ \rightleftharpoons HOCl$

B) $-\overset{\|}{C}-\overset{|}{N}H + HOCl \rightleftharpoons -\overset{\|}{C}-\overset{|}{N}-Cl + H_2O$

C) $-\overset{\|}{C}-\overset{|}{N}Cl \xrightarrow{\Delta} HCl +$ decomposition products

D) $HCl +$ "Fabric Bases" $\rightarrow$ "Fabric Bases"$\cdot HCl$

E) Cellulose $\xrightarrow[\text{"Fabric Bases"}\cdot HCl \text{ or } HCl]{\Delta}$ Degraded Cellulose

Reactions A and B are involved in chlorine retention, and it can be seen from the equations that the amount of chlorine retained by a fabric will be determined by the concentration of hypochlorite ion in the chlorination bath, the pH of the bath, the number of $-\overset{\|}{C}-\overset{|}{N}H$ groups present in the resin on the fabric, the equilibrium constant of Reaction B for the particular resin and at the particular temperature involved (provided that the fabric is in the chlorination bath long enough for equilibrium to be established), and the rate or equilibrium constant of the reverse of Reaction B depending upon the method of rinsing if rinsing after chlorination is involved. In addition, the decomposition rate of the chloroamide at room temperature must be taken into account if chlorine retention is to be measured a considerable length of time after chlorination takes place. In chlorine damage where Reactions A through E are involved, the degree of damage will be determined by the degree of chlorine retention, the rate of Reaction C at the temperature of scorching, the strength of the fabric bases or the acidities of their hydrochlorides, the rate of Reaction E at the scorching temperature, and the time of scorching. In the AATCC test for chlorine damage, where many of the variables listed above are held constant, the determining factors become the number of $-\overset{\|}{C}-\overset{|}{N}H$ groups present in the resin on the fabric, the equilibrium constant of Reaction B, the rate of reverse Reaction B, the rate of Reactions C and E, and the strength of the fabric bases. With this background, several conceivable modes of action by which a chlorine damage depressant might act to reduce chlorine damage as measured by the AATCC test can be seen. It might react with the resin to tie up $-\overset{\|}{C}-\overset{|}{N}H$ groups, making them unavailable for chloroamide formation, and apparently certain epoxy compounds and formaldehyde function in this manner. A depressant might also in some way affect the rates and equilibrium constants of Reactions B and C so that the chloroamide formed would be hydrolyzed during the rinsing step of the test or so that the chloroamide would not liberate acid during the scorching step. Apparently no depressants of this type are known at the present time, although as Nuessle has pointed out, differences in chlorine damage shown by urea and melamine resins are due at least in part to the slower rate of Reaction C in the case of the melamine resins. A depressant might also function by fixing to the fabric or the resin groupings which are basic enough so that their hydrochlorides are not acidic enough to cause appreciable fabric damage during the scorching step of the test. Apparently alkaline salts precipitated within the fabric, sodium carboxymethyl or carboxyethyl groups fixed on the fabric, certain triazine resins, and the triazone resins function at least partially in this manner. Depressants which function because of their basicity will effectively prevent chlorine damage only if the basic material is fixed to the fabric in sufficient concentrations to neutralize the acid liberated due to the chlorine retention of the

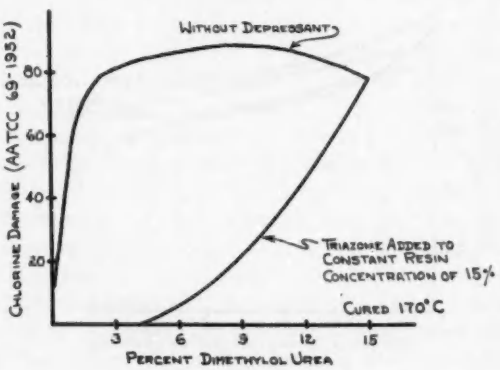


Fig. 5.

resin present. Some resins, such as certain of the triazine resins, although they are basic, do not always show low chlorine damage because they retain more chlorine than their basic sites can neutralize when it is liberated as hydrochloric acid. Many potential depressants of the basic type are unsatisfactory. In some instances this is because when they are mixed with chlorine-retentive resins and the mixture is applied to fabric and cured, the resins are cured before the depressant is fixed to the fabric or the resin; therefore low chlorine damage is not assured. With the straight triazone resins, the basic grouping is part of the resin molecule, so that if the resin is fixed the basic group is also fixed, and low chlorine damage is assured under all conditions of resin application or laundering of the finished fabric. With the mixed triazone resins, where all of the chlorine-retaining groups are not attached to the basic molecule, apparently the reaction rate of the triazones with the methylol ureas and with the fabric is fast enough to insure complete freedom from damage from retained chlorine even under very mild curing conditions with mixtures containing a high percentage of triazone, in the order of 75% or more. To enable the use of a high amount of DMU such as a 1:1 mole ratio, it is desirable to use a fairly thorough cure to insure low chlorine damage in the treated fabric, especially after severe laundering. The chlorine damage depressant effect of the triazone resins on urea formaldehyde resins, dimethylolethyleneurea, and tetramethylol acetylenediurea is graphically illustrated in Figures 5, 6, and 7. The only mixtures to have become commercially important to date have been the urea formaldehyde-triazone mixtures.

The durability of a creaseproofing finish to laundering and to acid souring as normally encountered in home and commercial laundering is an important fabric property. Here again, as in the case of the physical properties of the fabric, the durability of the finish will depend not only upon the type of finish but also upon the conditions of application of that finish. Resin finishes which have been well cured are more durable than those which have been only superficially cured. The durability of the better triazone resins, when properly cured, compares favorably with that of other nitrogenous resins; however, some of the non-nitrogenous creaseproofing treatments such as the acetals and epoxies are more durable than any of the nitrogenous resins. Figure 8 shows the effect of 20 automatic home launderings

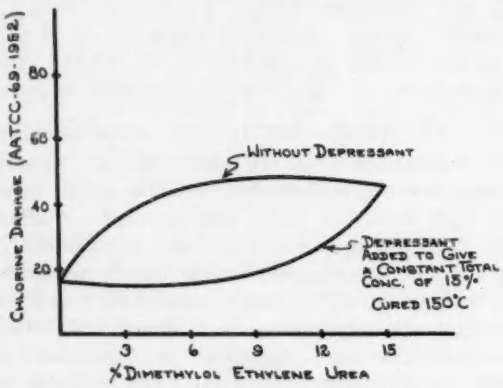


Fig. 6.

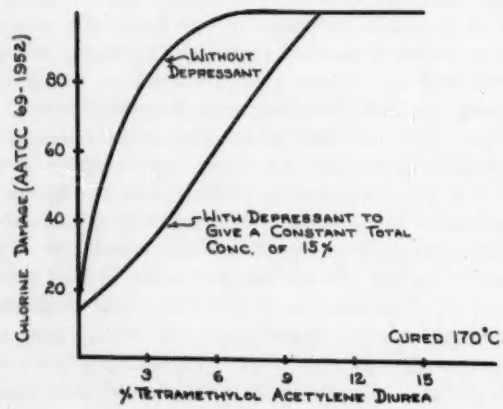


Fig. 7.

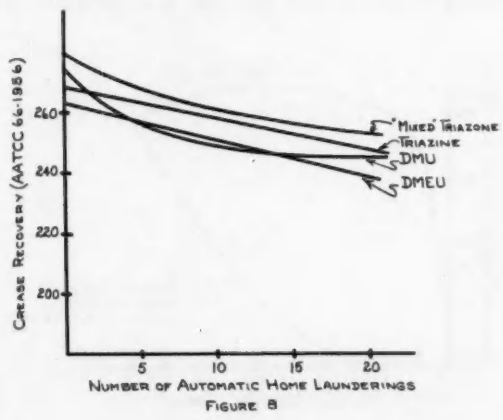


Fig. 8.

TABLE III

Type finish	Reflectance	
	Initial	Clorox and Tide, 5 washes
Mixed triazone	87.6	89.0
Cyclic urea	86.8	88.6
Triazine-cyclic urea	87.0	82.8
No resin	88.1	88.3

on the crease resistance of fabrics treated with various types of resins. Figure 9 shows the effect of 20 commercial white work washes on the crease resistance of fabrics treated with a mixed triazone resin, dimethylolethylene urea, and a dimethylolethyleneurea-triazine resin combination.

Commercial laundries normally employ a final acid sour as part of their laundering procedure, which has a tendency to remove resins from the fabric. In order to study the effect of souring apart from the other factors involved in commercial launderings, fabrics treated with various resins were repeatedly subjected to acid souring conditions. When the souring procedure was carried out as recommended by the American Institute of Laundering, that is, at pH 5 for 3 min. at 100° F., the crease resistance of all of the fabrics was almost unchanged after 15 repetitions of the souring operation. When the more severe souring conditions of pH 3.4 with sodium silicofluoride at 120° F. for 5 min., such as might be encountered in poor laundry practice, were employed, crease resistance was reduced considerably, as shown in Figure 10. The triazone resin seems from this data to be more resistant to the conditions of acid souring than the other resins tested.

The tendency of finished fabrics to discolor is another fabric property in which there is great interest today. There are so many possible causes of fabric discoloration that considerable confusion exists concerning this property. Some of the instances in which discoloration of resin treated fabrics have been known to occur are during the curing of the resin, during hypochlorite bleaching, on aging, on exposure to alkalis, on exposure to heat, on exposure to heat after hypochlorite bleaching, or during laundering due to wet soiling. The tendency of fabrics treated with the triazones to yellow under certain conditions may be attributed to the instability of these compounds at high temperatures, especially under acidic conditions. Thus fabrics treated with

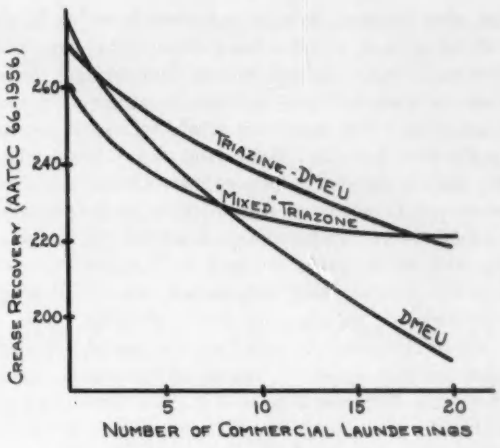


Fig. 9.

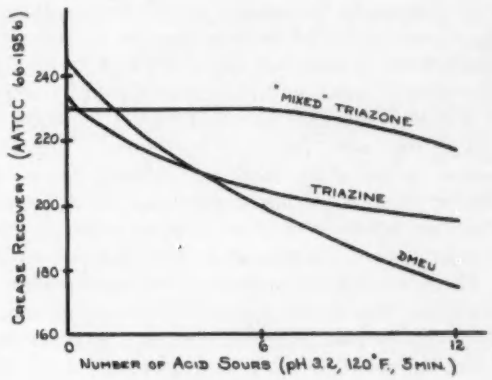


Fig. 10.

triazone resins tend to yellow when cured at high temperatures, when scorched at high temperatures, such as in the Suter Scorch Test at 400° F. for 30 sec., and when scorched after chlorination, as in the AATCC Tentative Test Method 69-1952. In no case is the discoloration indicative of an accompanying loss in fabric strength, and in each case the discoloration is easily removed by hypochlorite or peroxide bleaching. Fabrics treated with triazone resins do not discolor on repeated hypochlorite bleaching as do fabrics treated with even the best of the triazine resins or triazine resin mixtures, nor do they discolor on aging or on treatment with strong alkalis as do the ketone-aldehyde and dialdehyde type finishes. Although almost every type of resin finish has been accused of wet soiling during launder-

ing at some time, no case is known in which fabric treated with a thermosetting resin alone has been proven to pick up soil during laundering. Most cases of discoloration by resin treated fabrics on laundering which have been attributed to wet soiling by the resin have been due to soil pickup by an additive such as durable water repellents, latices, silicones, or polyethylenes, or to discoloration by the resin or an additive by treatments accompanying the laundering such as bleaching or pressing. Certain types of optical bleaches may sometimes cause yellowing which may be mistaken for resin yellowing.

Table III shows the reflectances of samples treated with various types of resins as measured by a Photovolt Reflectometer with a blue filter initially and after five home launderings with a synthetic detergent and hypochlorite bleach.

One important difference between the type of yellowing shown by the triazines and the type of yellowing shown by the triazones is that the yellowing of the triazones behaves as one would expect any discoloration of cotton to behave; that is, when a fabric is discolored by excessive heat and is bleached to remove the color, the color is removed. The triazines, on the other hand, are yellowed by hypochlorite bleaches during laundering, and if further bleaching is employed in an attempt to remove the discoloration, it is aggravated rather than removed.

The mixed triazone resins show much less tendency to discolor than do the straight triazone resins under all conditions where discoloration has been observed. Some, but not all, of the yellowing of the commercial triazone resins can be attributed to impurities, since resins prepared from carefully purified triazones show less yellowing than the commercial products; however, the discoloration at high temperatures is still considerable.

It has been suggested [1, 7] that fabrics treated with triazone resins have a tendency to develop odor. Since there are so many types of odor associated with textiles, no satisfactory method of quantitatively measuring all types of odor has yet been devised; therefore, fabric odor remains in the category of properties which can be measured only subjectively. Thus, it is impossible to cite figures to show whether fabrics treated with triazone resins have more or less odor than fabrics treated with other creaseproofing agents; however, it may be helpful to cite certain facts about the triazones which may have a bearing on the odor problem.

Samples of pure triazones, which are odorless, white, crystalline materials, have been kept at room temperature for more than five years without decomposition or odor development, indicating that the triazones themselves are quite stable compounds. They can be recovered unchanged after being held at room temperature for 24 hr. in dilute sodium hydroxide solution or in 10% hydrochloric acid. Judging from the stability of the parent triazones, it would be expected that the triazone resins, when free from impurities, would have little odor. Experience has indicated that any fabrics treated with resin should be washed to avoid the possibility of odor formation. Triazones are no exception. Likewise, as with other resins, improper manufacture, leaving impurities in the product, may tend to increase the danger of odor problems.

Since many commercial triazone resins contain considerable amounts of free formaldehyde, formaldehyde odor both in processing and on the finished fabric is often a problem. Where there have been customer complaints on odor with the triazone resins, the odor generally has been formaldehyde odor and not amine odor, and the complaints have been largely from cutters or retail stores where large amounts of resin treated fabrics have been stored in poorly ventilated spaces. Formaldehyde odor complaints in general, however, have not been predominately from fabrics treated with triazone resins, but from fabrics in general which have not been washed well or at all after curing, irrespective of the type of creaseproofing agent. Some of the triazone resins which contain very large amounts of free formaldehyde, however, call for exceptionally thorough washing of the treated fabric in order to avoid formaldehyde odor. In short, all fabrics finished with nitrogenous resins should be washed, and thoroughly washed fabrics treated with triazone resins do not develop objectionable odors during normal usage.

In the final analysis, the proof of any fabric finish is in large scale commercial usage. The triazone resins have now had that usage and have been found to be a valuable addition to the finisher's line of creaseproofing materials. Hundreds of millions of yards of fabric have been treated with triazone resins and have been found to perform satisfactorily in use. The past several years have seen resin finishing of white shirting and sheeting for the first time, and triazone resins have been used on a large percentage

of these fabrics. Triazone resin finishes have been approved by the American Institute of Laundering.

To be sure, the triazone resins are not cure-alls or the ultimate in creaseproofing agents. Their use is indicated wherever high crease resistance with good fabric strength without danger of strength loss or discoloration on chlorine bleaching is desired. Their use is not indicated where fabrics are not to be washed after treatment, where extremely high curing temperatures must be used, or where the finished fabric is apt to be subjected to high temperatures, such as in the manufacture of fused collars.

It is probable that the performance of the triazone resins will be improved in the future as new modifications of the resins are made and new catalytic systems are perfected. Finishers are learning that creaseproofing agents can be blended to give results which are superior to those given by individual agents much as fibers are blended to give improved fabric properties, and new additives to resin formulations are being discovered which can minimize certain resin deficiencies. No doubt entirely new types of creaseproofing agents will be developed in the future which will overcome the weaknesses of the triazone resins. Already new resins based on methylol tetrahydropyrimidones have been developed which have the complete freedom from chlorine damage of the triazone resins without odor or discoloration problems. Some of the cross-linking agents not involving formaldehyde such as certain aziridinyl compounds, epoxy compounds, and halohydrins are showing promise. In spite of the promises of new developments on the horizon, however, it seems probable that the triazone resins will remain one of the useful tools of the resin finisher for a long time to come.

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Performance Characteristics of a New Triazine-Formaldehyde Based Cross-Linking Agent for Cellulosic Fabrics[1]

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Introduction

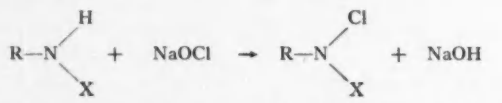
Urea, Melamine, and Ethylene Urea Formaldehyde

Urea formaldehyde was the first commercially important product for imparting wrinkle recovery to cellulosic fabrics. Fabrics finished with this product are characterized by such disadvantages as poor resistance to acid hydrolysis, poor durability, and strength loss when washed with chlorine bleach.

The introduction of melamine formaldehyde provided a finish with improved durability, resistance to strength loss during chlorine bleaching, and resistance to acid hydrolysis. The earlier melamine formaldehyde finishes had the disadvantage, however, of yellowing when washed with chlorine bleach.

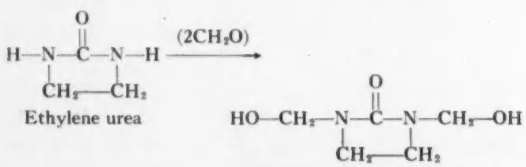
The introduction of ethylene urea formaldehyde was the next step in the development of an improved chlorine resistant finish of commercial importance.

The generally accepted mechanism for chlorine retention [7] with an aminoplast is the formation of a chloramide or chloramine as shown below.



Aminoplast — Sodium hypochlorite — Chloramide or chloramine — Sodium hydroxide

In the case of ethylene urea formaldehyde, decreased chlorine retention was obtained by blocking the nitrogens.



Ethylene urea — Dimethylolated ethylene urea

In practice, a large excess of formaldehyde is required to completely methylolate ethylene urea, resulting in objectionable excess free formaldehyde in the product. As a consequence, the nitrogen in commercial products may not be completely blocked, due either to incomplete reaction between the ethylene urea and formaldehyde or to loss of methylol groups during the curing step. The strength loss caused by chlorine retention is dependent on the ratio of methylol groups to ethylene urea in the treated fabric. This ratio determines the extent to which the nitrogen groups are blocked.

Figure 1 shows the strength loss as determined by the AATCC Accelerated Chlorine Retention Test for methylolated ethylene urea at different molar ratios of combined formaldehyde to ethylene urea.

Ethylene urea formaldehyde has poor resistance to hydrolysis during high temperature laundering and during the acid souring step in commercial washing. Hydrolysis results in increased retention of chlorine.

[1] Presented at the Chemical Finishing Conference of the National Cotton Council, October 2, 1958 at Washington, D. C.

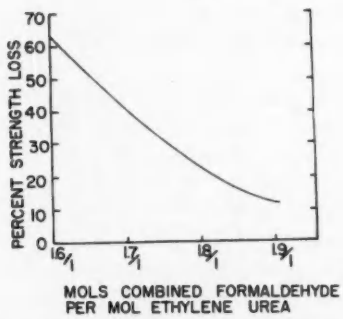
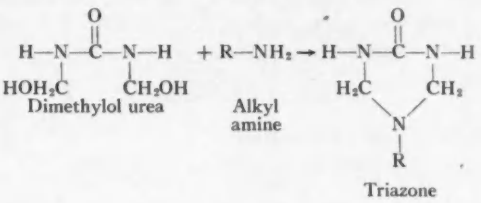
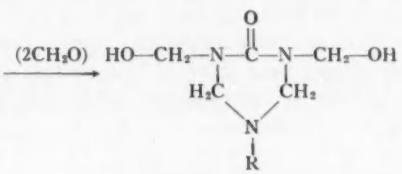


Fig. 1. Mol ratio vs. AATCC chlorine retention strength loss; methylol ethylene urea.

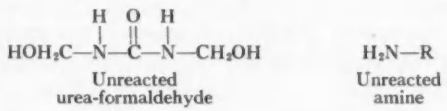
Triazone Formaldehyde

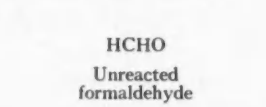
The introduction of tetrahydro triazone formaldehyde was the next step in producing a commercially important product with reduced chlorine retention. Blocking of the nitrogen was accomplished through the formation of a ring and subsequent methylolation by reacting dimethylol urea with a primary amine [9].

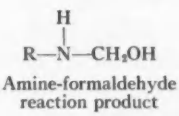




In commercial practice, the reaction between the amine and the dimethylol urea is not complete. The final reaction product also contains unreacted urea formaldehyde [9], free amine, and free formaldehyde, and probably reaction products of the amine and formaldehyde as shown.







The unreacted formaldehyde and alkyl amine are the source of formaldehyde and fish odors, respectively. The unreacted urea formaldehyde may result in discoloration by scorching and high strength loss after hot washes with bleach.

In this paper, the triazone formaldehyde product discussed will be ethyl tetrahydro triazone and will be designated as triazone. Triazones have slightly more resistance to acid hydrolysis than ethylene urea; however, they can also be hydrolyzed by high temperature washes with bleach alone or with bleach followed by acid souring.

Triazine Formaldehyde

The latest development in producing a chlorine resistant finish with improved resistance to acid hydrolysis is the introduction of a new multifunctional, triazine-formaldehyde-based cross-linking agent (Aerotex Resin 23 Special). This product will be referred to as triazine in this paper. In common with finishing agents based on melamine formaldehyde, it has excellent resistance to laundering and to acid hydrolysis. Unlike the early melamine formaldehyde products, the nitrogens are blocked. Strength loss due to chlorine retention is very low, both initially and after repeated laundering. Finished fabrics show no significant yellowing under practical laundering conditions.

The data to be presented will show the performance characteristics of this new triazine-based cellulose reactant. Comparisons of some of these properties with those of ethylene urea formaldehyde and triazone formaldehyde will also be made.

Wrinkle Recovery

It has been postulated that wrinkle recovery in cellulosic fabrics is obtained by cross-linking adjacent cellulose chains [3]. In addition, the hypothesis has been advanced that the length of this cross link has an effect on the relationship between wrinkle recovery and tensile strength [4]; that is, the longer the cross link the less loss in strength for an equal increase in wrinkle recovery. The length of this cross link may be a function of (1) the initial molecular size of the reactant, (2) the functionality of the cross-linking agent, and (3) the relative rates of reactivity of the cross-linking agent with itself and with cellulose. A compound with a high functionality has many reactive groups. It may polymerize to some extent before cross-linking the cellulose. This polymerization would result in a longer cross link between adjacent cellulose chains and consequently less loss in tensile strength with increasing wrinkle recovery.

The new triazine-based reactant is a relatively large multifunctional cross-linking agent. Therefore, it would be expected that a wide range of wrinkle recovery values with only moderate decreases in

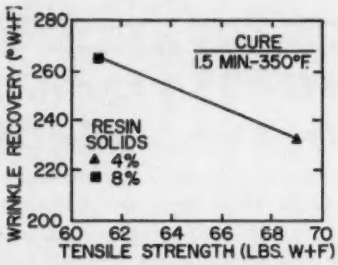


Fig. 2. Wrinkle recovery vs. tensile strength; triazine.

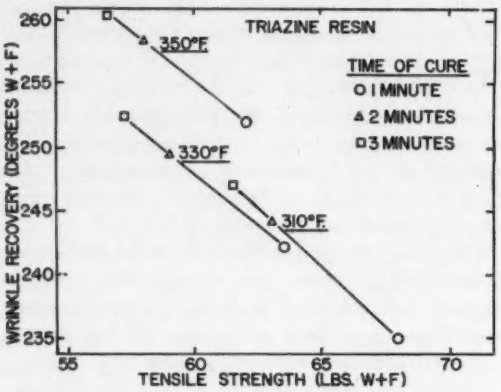


Fig. 3. Wrinkle recovery vs. tensile strength; triazine.

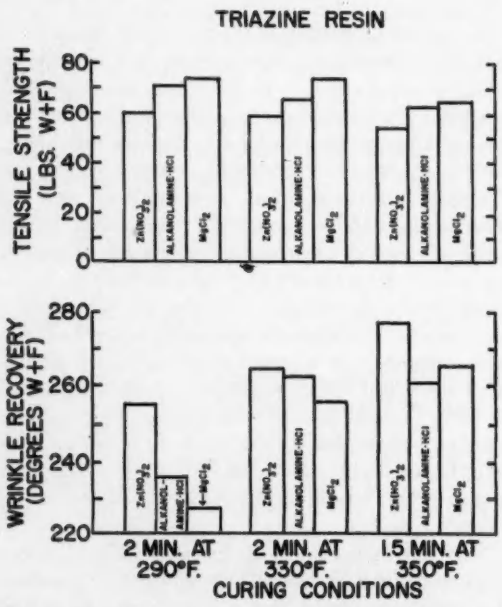


Fig. 4. Effect of cure and accelerator on wrinkle recovery and tensile strength; triazine.

tensile strength would be obtained by varying the solids applied or by varying the curing conditions.

Effect of Variation in Resin Concentration

Figure 2 shows the relationship between initial wrinkle recovery and tensile strength of triazine treated fabric at 4% and 8% solids add-on.

These data show that as the solids applied to the fabric were increased from 4% to 8%, the wrinkle recovery was increased from 232° to 266° with only an 8-lb. decrease in the tensile strength of the warp plus filling.

Effect of Variation in Cure

Figure 3 shows the effect of curing conditions on the wrinkle recovery and tensile strength. A variation from 1 to 3 min. in time and from 310° F. to 330° F. in temperature resulted in a range of wrinkle recovery values from 235° to 262°. This change in wrinkle recovery was accompanied by a difference in strength of 10 lb.

Use of Different Accelerators

The effect of different accelerators at various conditions of cure on the wrinkle recovery and tensile strength is shown in Figure 4. In general, the zinc nitrate type of accelerator produced higher wrinkle recovery at the three curing conditions with correspondingly lower tensile strength values. At the 330° F. cure, the wrinkle recovery obtained with zinc nitrate was only 10° higher than that produced with magnesium chloride; however, the tensile strength of the fabric containing magnesium chloride was 15 lb. higher. These data indicate that the use of magnesium chloride and curing at 330° F. will produce a finish with a good wrinkle recovery–tensile strength relationship.

Durability

Laundering. The durability of wrinkle recovery obtained with the triazine is very good, as shown in Figure 5. This graph shows that the durability was good in all cases, but at higher cure temperatures better durability was obtained.

Acid Hydrolysis. The relative resistance of finishes of ethylene urea, triazone, and triazine to acid hydrolysis is shown in Figure 6; 78% of the triazine-based finish was retained through the high tempera-

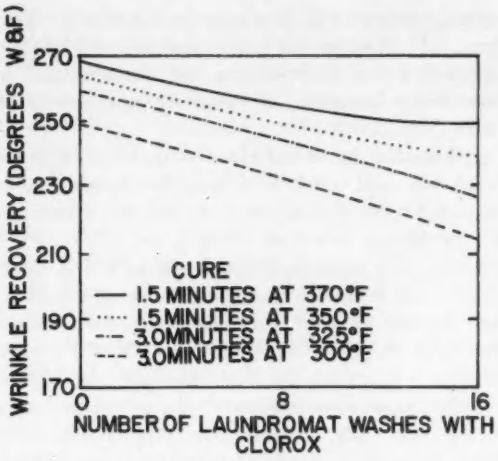


Fig. 5. Durability of wrinkle recovery; triazine.

ture acid hydrolysis procedure. The other two finishes showed poor resistance to acid hydrolysis, with the ethylene urea showing the greatest hydrolysis.

Wet Wrinkle Recovery

A fabric property that has received considerable attention recently is wet wrinkle recovery. Figure 7 shows the change in wet and dry wrinkle recovery of triazine-treated fabric with increasing solids add-on. This graph shows that as the resin solids of the triazine were increased, both the wet and dry wrinkle recovery were increased.

The bar graph in Figure 8 shows the results of an evaluation of appearance after washing of fabrics having varying wet and dry wrinkle recovery values. The appearance ratings of these samples after drip drying and after tumble drying are shown. This evaluation was made by comparing the appearance of two samples at a time until each sample had been compared with every other. The more times a sample was considered to have a better appearance than another, the higher was its ratings. This method of rating is similar to that used in ranking baseball teams on a win or lose basis. The samples that had both high wet and dry wrinkle recovery had the best appearance rating. The sample that had high wet wrinkle recovery and low dry wrinkle recovery was rated third in appearance after drip drying; however, the appearance of this sample after tumble drying was very poor.

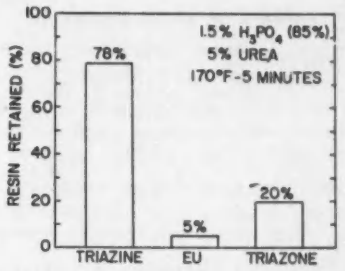


Fig. 6. Durability of finishes to acid stripping.

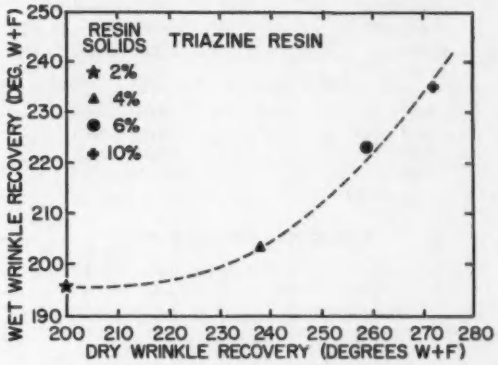


Fig. 7. Wet vs. dry wrinkle recovery; triazine.

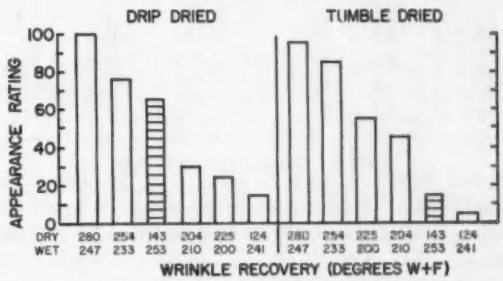


Fig. 8. Appearance rating vs. wet and dry wrinkle recovery.

These data show that high wet and dry wrinkle recovery are needed to obtain good minimum care appearance after laundering followed by tumble drying.

Chlorine Retention

Test Methods

There is no generally accepted test method for evaluating the effect of chlorine bleaching. There are, however, scores of different test methods to determine the effect of chlorine retention on resin-

TABLE I. Available Chlorine, %

	Based on liquor volume	Based on dry fabric weight	Bleach temp.	Liquor/ cloth
Commercial laundry	0.01	0.04	150–160° F.	4/1
Home laundry	0.02	0.26	120° F.	13/1
Stain removal	5.0	—	Room	—

TABLE II

Initial conc. of available chlorine, %	Conc. of available chlorine after 3 min., %
0.02	0.0045–.0065
0.01	0.0020–.0035
0.005	0.0017–.0025
0.002	0.0007–.0013

TABLE III. Triazine Resin

	Yellowness index				
	Commercial			Laboratory	
No. of washes	Power	Self service	Home	Laundromat, 140° F.	Najort, 160° F.
5	0.84	—	1.0	1.5	4.0
10	0.96	—	1.0	1.6	—
16	—	—	1.1	2.6	—
20	1.7	—	1.4	—	—
25	—	2.5	—	2.9	—
50	2.4	—	—	—	—

treated fabrics. Some of these tests are based on reliable data. Unfortunately, too many are based on incomplete information and serve to prove a specific point rather than serve as a realistic method of evaluation.

The major problem in developing an accelerated test method is the great variety of washing procedures. An accelerated test may be defined as one that is conducted under conditions which speed up the changes noted under practical or realistic conditions, which may be milder. If a test causes changes that do not take place under practical conditions, it is not an accelerated test but may be defined as an abusive test. In developing an accelerated test, it is necessary to find out what happens under practical conditions in order to determine whether the test is a realistic accelerated test or an abusive one.

Bleaching procedures can be divided into three general classes: (1) bleaching in commercial laundries, (2) bleaching in home washers, and (3) removal of stains. Conditions that may be used in these three methods of bleaching are shown in Table I.

Commercial and home laundry practice. It is believed that most commercial laundries bleach according to the recommendation of the American Institute of Laundering, shown in Table I.

In a typical home laundry, as shown in this table, twice as much chlorine based on the wash volume is used and six to seven times as much based on the weight of dry fabric. On the other hand, the temperature is lower and the liquor-to-cloth ratio higher.

Although various concentrations of chlorine may be used for stain removal, concentrated household bleach containing about 5% chlorine is often used. Stain removal is ordinarily carried out at room temperature.

There is one important condition that is common to both commercial and home laundering. These operations are carried out with a dirty load. Laboratory test washes are usually done with a clean load.

Laboratory washes. Test washes in the laboratory can vary in many ways, such as the type and amount of soil, if any, pH of the wash, ratio of load to liquor, temperature of the wash, and bleach concentration.

The change in chlorine concentration during clean load and soiled load laboratory washes at 140° F. is shown in Figure 9. In the clean load there was chlorine available through the first 10 min. of the laundering cycle. After the first minute of washing in the soiled load, only 25% of the original chlorine concentration remained. After 2 min., the amount of available chlorine was negligible.

The rate of decomposition of bleach in a commercial laundry is also very rapid. As shown in Table II [7], 50–75% of the available chlorine was used up in commercial laundering in a dirty load within the first 3 min., even though most of the soil was removed by previous sudsing operations.

It is to be expected that chlorine will oxidize the dirt in a dirty wash load and consequently be reduced. In a dirty load of resin-treated fabric, it would be expected that the chlorine would first oxidize the dirt in the wash liquor and on the surface of the fabric before diffusing inside the fiber and chemically reacting with the resin. Since it has been shown that the available chlorine in a dirty load is rapidly reduced, the chlorine available to

react with the resin is much smaller than the amount originally introduced in the wash liquor.

The change in pH during clean and soiled load washes is shown in Figure 10. The pH remained at 9.5 during the first 10 min. of the clean load wash. In the soiled load wash, the pH dropped from 9.5 to 7.8 in 1 min. and to 7.3 in 10 min.

The cloth-to-liquor ratio has an effect on the change in chlorine concentration and pH during the washing cycle, as shown in Figure 11. At the smaller load-to-liquor ratio, the percent of available chlorine and pH remained fairly constant. At the higher ratio, the percent of available chlorine and pH decreased faster.

Discoloration

Effect of various laundering procedures. The resistance of the triazine finish to yellowing during chlorine bleaching was determined by subjecting treated fabric to several types of practical launderings and laboratory wash tests.

The data presented in Table III were obtained on a wide variety of fabrics gathered from mill trials and laboratory applications. A variety of accelerators, curing conditions, and additives were used on these fabrics. The values are based on the averages of several hundred fabric samples. The commercial and home washes were done with a soiled load. The laboratory washes were run with a clean load and 0.02% available chlorine.

A fabric that has a yellowness index of 3 or less appears white unless compared against a whiter standard. The discoloration of a fabric with a yellowness index greater than 5 can be seen without a standard. The highest yellowness index values obtained under actual commercial conditions were 2.4 after 50 launderings in a commercial laundry and 2.5 after 25 launderings in a self-service laundry.

The laboratory procedure which produced a similar yellowness index value was 16 Laundromat washes at 140° F. Therefore, 16 Laundromat washes with a clean load at 140° F. may be considered sufficient for reproducing the yellowing obtained in 50 commercial washes or 25 self-service washes of soiled fabrics.

The highest yellowness index value obtained in 20 home launderings with a dirty load at 120° F. was 1.4. The laboratory procedure which produced a similar index was 5 Laundromat washes at 140° F. with a clean load. Five Laundromat washes, there-

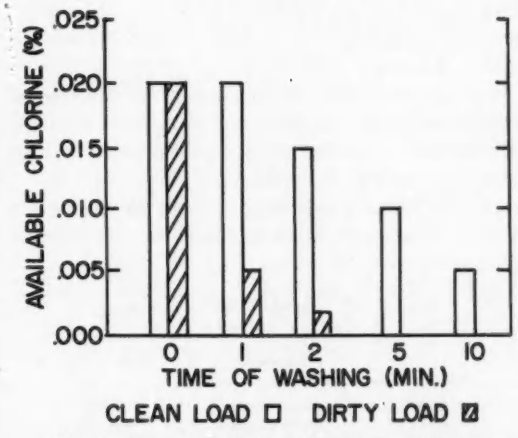


Fig. 9. Clean vs. soiled load laundering; effect on available chlorine.

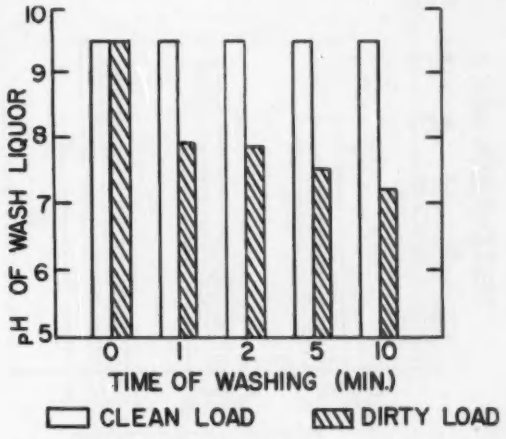


Fig. 10. Clean vs. soiled load laundering; effect on pH.

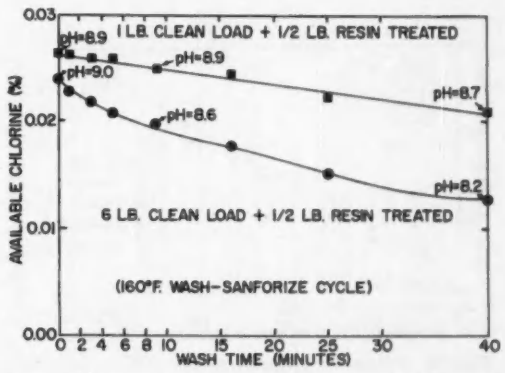


Fig. 11. Effect of load-to-liquor ratio on available chlorine.

fore, represent a suitable test for reproducing 20 home launderings.

It is important to note that the highest yellowing index obtained in all the practical washes made was 2.5, which is not significant yellowing.

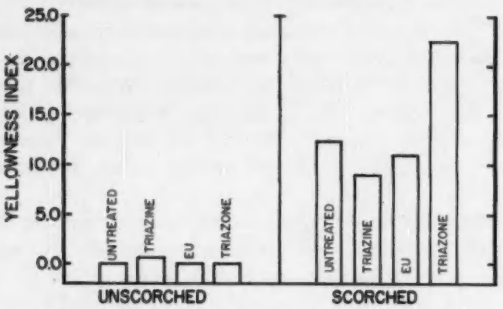


Fig. 12. Effect of concentrated bleach on yellowness index.

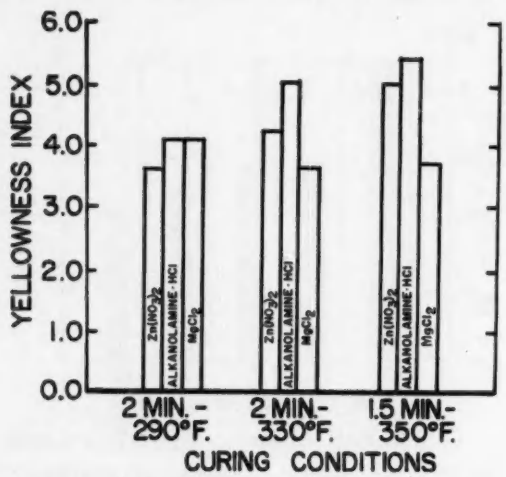


Fig. 13. Effect of accelerator and cure on yellowness index; triazine.

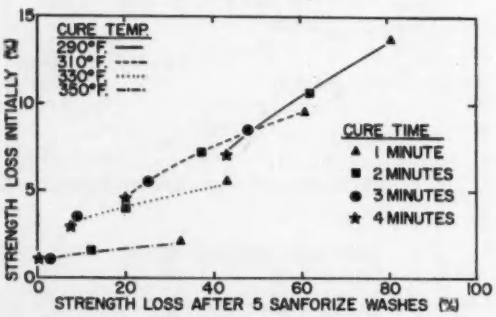


Fig. 14. Effect of cure on AATCC chlorine retention initially and after laundering.

Laboratory washes at 160° F. using a clean load, detergent, and chlorine produced a yellowness index of 4 after 5 washes. Although this value is relatively low, it is considerably higher than obtained after 25 washes in a self-service laundry or 50 washes in a commercial power laundry.

It appears that 160° F. washing with chlorine using a clean load may be, however, a suitable accelerated wash test. Further study of variations in the number of wash cycles, bleach concentrations, and other factors in the 160° F. wash is needed, however, to establish it as a realistic and accelerated test for chlorine retention.

Stain removal. In order to determine the effect of bleaching with concentrated household bleach, as is often used in stain removal, untreated cotton fabric and fabrics treated with triazine, ethylene urea, and triazone were immersed in household bleach containing 5% available chlorine for 30 min. at room temperature. The samples were then given a Laundromat wash at 140° F. with bleach and then scorched.

As can be seen in Figure 12, soaking in concentrated household bleach did not cause any of the fabrics to yellow significantly.

After being scorched, the triazine-treated fabric yellowed the least. The ethylene urea-treated and untreated fabrics yellowed slightly more. The triazone-treated fabric discolored badly. The discoloration noted in the triazone fabric may have been caused by the presence of urea formaldehyde.

Effect of different accelerators. Figure 13 shows the effect of the choice of accelerator and curing temperature on the tendency to yellow after 5 accelerated washings with a clean load, Tide, and 0.02% chlorine at 160° F.

As can be seen, the finishes with magnesium chloride showed less yellowing than those with the zinc nitrate or alkanol amine hydrochloride type of accelerator at 330° F. and 350° F.

Discoloration by scorching. Table IV shows the results of a scorch test on cotton fabrics finished

TABLE IV. Discoloration by Scorching (30 Sec. at 365° F.)

	Initially	After 5 washes
Untreated	Very slight	Very slight
Triazine	Very slight	Very slight
EU	None	Very slight
Triazone	Very slight	Yellow

with triazine, ethylene urea, and triazone after 5 washes at 160° F. with 0.02% chlorine.

The degree of discoloration of the triazone finish was similar to that which is obtained with a urea formaldehyde finish. This discoloration may be explained by the presence of urea formaldehyde in the triazone or its formation on the fabric from the rupture of the triazone ring.

Strength Loss Due to Chlorine Retention

Effect of curing conditions. Figure 14 shows the strength loss of triazine-treated fabric caused by retained chlorine as measured by the AATCC Accelerated Chlorine Test [1] initially and after five washes at the boil without chlorine.

The range of curing conditions was varied from 1 to 4 min. at temperatures from 290° F. to 350° F. In all cases the initial strength loss as determined by the AATCC test was less than 15%. Longer curing time and higher curing temperature tend to decrease this strength loss.

Although high strength losses after washing were obtained on fabrics cured less than 2 min. at 310° F., this loss was reduced considerably at longer times or higher temperatures of cure. Excellent resistance to strength loss after washing was obtained on fabrics cured longer than 2 min. at temperatures of 330° F. or higher. This curing condition represents a good one for optimum properties in general.

Effect of different accelerators. The effect of choice of accelerator and curing conditions on the strength loss of the triazine-treated fabric as determined by the AATCC Chlorine Rentention Test initially and after high temperature washing is shown in Figure 15.

In general, the zinc nitrate type accelerator produced finishes with the lowest strength loss initially and after high temperature washes. The alkanol amine hydrochloride accelerator generally showed the most strength loss. Magnesium chloride gave satisfactory results if the finish was cured at least 2 min. at 330° F. The zinc nitrate type accelerator is recommended when lower temperature curing is used as far as retention of strength as measured by the AATCC test method after washing at 212° F. is concerned.

Comparison of commercially important finishes. The effect of washing without chlorine bleach on the strength retention as measured by the AATCC Accelerated Chlorine Retention Test is illustrated in Figure 16.

Both the triazine and triazone finishes showed excellent resistance to chlorine retention initially and after washing. However, the ethylene urea finish showed low strength retention as determined by the AATCC Chlorine Retention Test after laun-

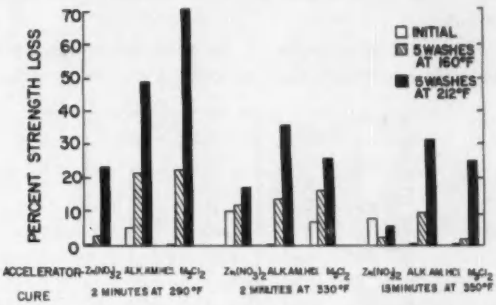


Fig. 15. Effect of accelerator and cure on AATCC chlorine retention initially and after laundering; triazine.

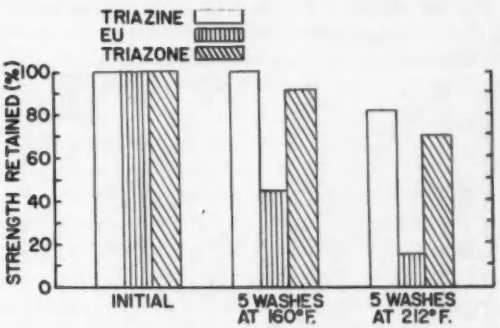


Fig. 16. AATCC chlorine retention on different finishes initially and after laundering without bleach.

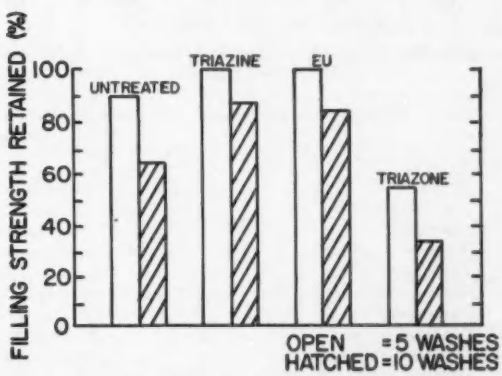


Fig. 17. Effect of laundering with bleach on tensile strength of different finishes.

dering without bleach, especially at high temperature washing.

The effect of high temperature laboratory washing in the presence of chlorine bleach on strength retention is shown in Figure 17. As can be seen, the triazone finish exhibits a high loss in strength under this condition of test, which does not include scorching, while the ethylene urea and triazine show very little loss.

The loss in strength of the triazone under these washing conditions may be caused by the presence of urea formaldehyde or its formation on the fabric from the breaking of the triazone ring in the presence of hot chlorine bleach.

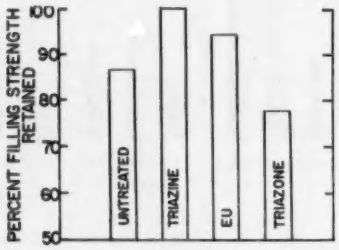


Fig. 18. Effect of 20 commercial launderings on tensile strength of different finishes.

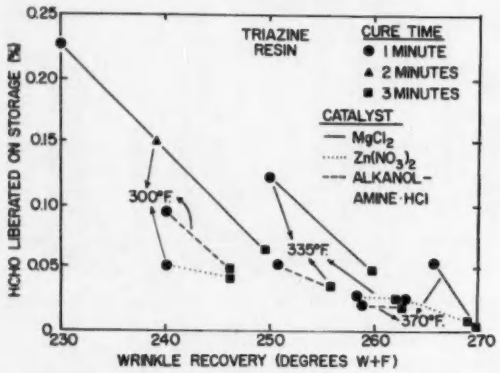


Fig. 19. Effect of accelerator and cure on HCHO liberation; triazine.

The strength loss noted after chlorine washes in the laboratory was confirmed by commercial washes, as shown in the bar graph in Figure 18.

The triazine- and EU-finished fabrics showed no significant loss in filling strength after 20 commercial washes with bleach and sour. The untreated fabric retained 87% of its original filling strength, while the triazone-treated fabric retained only 78% of its filling strength.

Soil Pick-Up During Washing

Some fabric finishes have a tendency to pick up and retain soil when washed in a dirty load [6]. Fabrics treated with a triazine finish with and without additives were tested for soil pick-up by washing in a commercial laundry, in a self-service laundry, and in a home washer using dirty loads. The percent reflectance of the washed fabrics is presented in Table V.

These data show that triazine-treated fabrics retain their original whiteness after repeated washes in commercial, self-service, and home laundries. The whiteness retention is equal to that of the untreated fabrics. The durable polyethylene, silicone, and thermoplastic additives, however, caused the finish to pick up soil. The thermoplastic additive was an acrylate resin. The acrylate additive gave, by far, the greatest soiling. The finish containing the nondurable softener did not retain soil, probably because the softener was removed during washing.

Odor Formation

The two principal types of objectionable odor normally associated with resin finishing of textiles

TABLE V

	Type of laundering						
	Commercial			Self service	Home		
	5	10	15	25	4	12	20
Untreated	97.1	91.9	93.2	—	97.2	92.5	93.4
Triazine	95.7	90.0	94.1	96.7	97.5	96.4	95.7
Triazine + silicone	90.8	86.6	90.5	89.2	—	—	—
Triazine + polyethylene	95.6	83.1	89.4	89.2	—	—	—
Triazine + thermoplastic resin	80.9	78.7	79.2	—	—	—	—
Triazine + nondurable softener	94.1	—	—	93.8	—	—	—

are the odor of formaldehyde and the odor of alkyl amines, commonly called "fish odor" [5]. These odors may be present in the product, during processing or in the finished fabric. Their presence in the fabric can be a serious deficiency.

Formaldehyde Odor

The problem of the liberation of formaldehyde during the storage of resin-treated goods has become increasingly important in recent years [2]. The amount of formaldehyde liberated is dependent on several factors, including the amount of free formaldehyde present in the product, the accelerator used, and curing conditions.

Accelerator and cure. Figure 19 shows the effect of the choice of accelerator and cure conditions on the amount of formaldehyde liberated from fabric treated with triazine. The following general conclusions can be made based on the data in this graph.

1. Those conditions which produced the highest wrinkle recovery also minimized formaldehyde liberation.
2. At the higher cure temperatures, all three accelerators are equally efficient in minimizing formaldehyde odor. Magnesium chloride is less efficient at lower cure temperatures and shorter cure times.
3. Cure temperatures of about 335° F. are required to get minimum formaldehyde liberation. The time of cure was not as significant a factor as the temperature in its effect on formaldehyde liberation.

Comparison of finishes. The percent of formaldehyde liberated from fabrics treated with triazine, ethylene urea, and triazone finishes is shown in Figure 20. The triazine finish liberated the least formaldehyde, and the ethylene urea finish generally showed slightly more formaldehyde liberation than the triazine. The triazone finish liberated the most formaldehyde under most of the cure conditions studied. The unreacted formaldehyde in the triazone may have contributed to the high amount of formaldehyde liberated from the fabric.

Alkyl Amine Odors

One of the causes of fish odor in treated fabrics is the presence of an alkyl amine in the finishing agent. Although triazones contain unreactive alkyl amine, as previously shown, triazine does not contain an

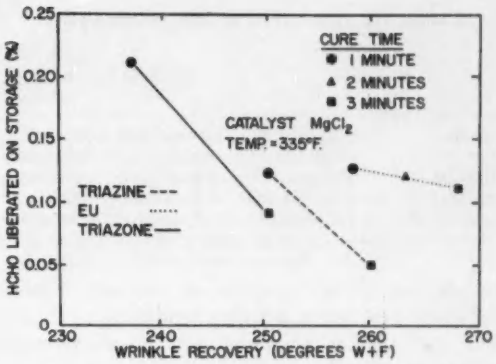


Fig. 20. Effect of cure on HCHO liberation of different finishes.

alkyl amine. Therefore, the presence of fish odor due to unreacted amine is not possible. In order to learn if triazine is capable of producing fish odor, fabrics were treated with triazine using a magnesium chloride accelerator. The treated fabrics were cured over a wide range of time and temperature, but were not afterwashed. An odor test was performed by smelling fabrics which had been moistened with water and stored in a sealed bottle overnight at room temperature. The results of the odor tests on these treated fabrics are presented in Table VI.

A fish odor was not detected in any of these fabrics. These results indicate that triazine may be used with a non-nitrogen containing metal salt accelerator without producing fish odors even without afterwashing. The elimination of afterwashing to reduce or remove fish odor represents an economic advantage. There have been no reports of fish odor on the millions of yards of fabric already treated with triazine.

Table VII shows the results of odor tests on fabrics treated in the mill with triazine, ethylene urea,

TABLE VI. Odor Test—Triazine Resin

Curing conditions		
Time, min.	Temperature, ° F.	Odor test
2.9	270	Negative
1.7	290	Negative
0.8	320	Negative
2.9	320	Negative
5.0	320	Negative
1.7	350	Negative
4.2	350	Sl. burnt
2.9	370	Sl. burnt

TABLE VII. Odor Tests on Mill-Treated Fabrics

	Water	1% Soda ash	AATCC alk. persp.
Triazine	Negative	Negative	Negative
EU	Negative	Negative	Negative
Triazone (1)	Fish odor	Fish odor	Fish odor
Triazone (2)	V. sl. fish odor	Fish odor	Fish odor
Triazone (3)	Negative	Negative	Negative

and triazone. The tests were carried out on fabric moistened with water, alkaline conditions (1% soda ash), and alkaline perspiration. The triazine and ethylene urea finishes exhibited no odor in these tests. Two of the three triazone-treated fabrics exhibited fish odor.

The triazone finish that did not have a fish odor was known to have received a thorough wash and perborate bleach. Since large-scale commercial use of triazone finishes is relatively recent, it remains to be seen if this tendency to produce fish odor will be noticed under use conditions where thorough washing is not done, or where odors build up in washing solution in continuous plant operations. With the triazone, there is also the possibility of rupture of the ring under drastic use conditions, which might free the amine and cause fish odor.

Summary

The performance characteristics of a new triazine formaldehyde-based cross-linking agent for cellulosic fabrics have been described. Some of its properties have been compared with those of two other commercially important finishing agents, ethylene urea formaldehyde and triazone formaldehyde. In addition, comparisons have been made of the effects of washing under actual use conditions with those of various laboratory test wash procedures.

Applied to cotton fabrics, this triazine-based cross-linking agent (Aerotex Resin 23 Special) provides a wide range of dry and wet wrinkle recovery values with only moderate decreases in tensile strength. The finish shows good resistance to chlorine, as measured by strength loss and discoloration under practical laundering conditions. It shows low soil pick-up during washing and is resistant to acid hydrolysis. This cellulose reactant inherently does not present a fish odor problem and exhibits a minimum of formaldehyde odor.

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Letters to the Editor

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Effect of Twist in Mercerization of Single Yarns

The Ahmedabad Textile Industry's
Research Association
Ahmedabad 9
India
October 8, 1958

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Corser and Turner [1] have investigated the effect of twist in mercerization of doubled yarns and found that the changes in breaking strength depend on singles and ply twists. They measured lea strength and single thread strength (on Baer and Moscrop instruments) and found that the results were sometimes conflicting. Effect of twist in mercerization of single yarns has received much less attention, probably because of its less commercial importance. Goldthwait [2] has quoted some results on 12s yarn at only two twist levels. We report here the results of a more detailed study on 60s yarn at six twist levels.

60s yarn was spun from Sudan mixing at following twists: 20, 24, 30, 36, 40, and 44 turns per inch. The yarn was scoured on a laboratory single package Thies dyeing machine. By using a 1-yd. length as a unit, a 150-yd. length of yarn of each twist was divided into two lots by throwing a coin to decide whether each 1-yd. piece should go to the first lot or to the second. This random distribution was adopted in order to minimize effects due to the variation in the yarn. One lot of each twist was kept unmercerized and the other divided into three portions. Each portion was mercerized on different days, along with similar portions from other twists. This procedure was adopted in order to minimize effects due to variations in the mercerization process.

The yarn was mercerized on a specially designed machine for treatment of single yarns, the details of which will be published elsewhere. In brief, single thread was passed successively through caustic soda solution of mercerizing strength (three dips), dilute acetic acid, and running water. After each passage through a solution, the yarn passed between squeezing rollers which were all driven positively from a common drive to keep the tension low. However, it was found that the yarn suffered about 1% extension during the treatment. Mercerization on this machine was expected to be much more uniform than mercerizing in hank form. 52° Tw caustic soda solution containing 0.5% Invadine ME was used at 15° C., the time of treatment being 2½ min.

The mercerized and unmercerized yarns were tested on an Instron Tensile Tester for breaking

TABLE I. Effect of Twist in Mercerization of 60s Yarn

Twist, t.p.i.	Increase in breaking strength on mercerization, %	Decrease in breaking elongation on mercerization, %	Barium activity number
20	20	35	192
24	10	25	192
30	9	12	183
36	2	20	177
40	1	15	168
44	−2	27	162

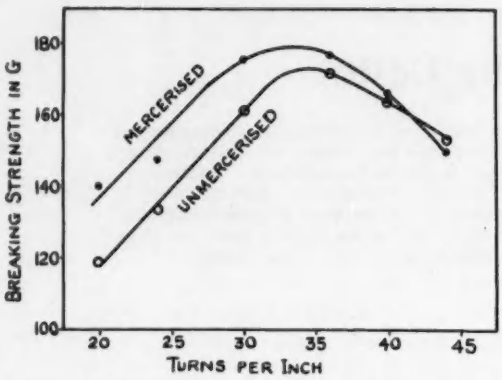

Fig. 1. Breaking strength vs. twist for unmercerized and mercerized 60s yarn.

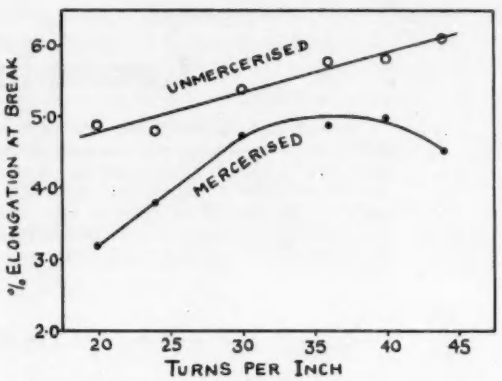

Fig. 2. Elongation at break vs. twist for unmercerized and mercerized 60s yarn.

strength and elongation, taking 102 readings for each sample. Barium activity numbers were also measured to see if the twist had made any difference in the extent of mercerization. The mean values of breaking strength and elongation are presented in Figures 1 and 2 respectively, and the percent changes in these properties, along with the barium activity numbers, are recorded in Table I.

It is seen from Figure 1 that the strength vs. twist curve has not shown much change in its shape except that the region of the optimum twist has become wider. The lowest twist has given the maximum percent increase in strength, which decreases with increasing twist. The highest twist has shown a small decrease in strength on mercerization. In the case of elongation (Figure 2), however, the shape of the curve itself has altered. The unmercerized yarn shows a linear relation between elongation at break and twist, but in the case of mercerized yarns the elongation at break has increased with increasing twist, reached a maximum, and then declined. The barium activity numbers indicate that the degree of mercerization decreases with increasing twist. This is to be expected, since higher twist will interfere with the penetration of the caustic and swelling and deconvoluting of the fibers.

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